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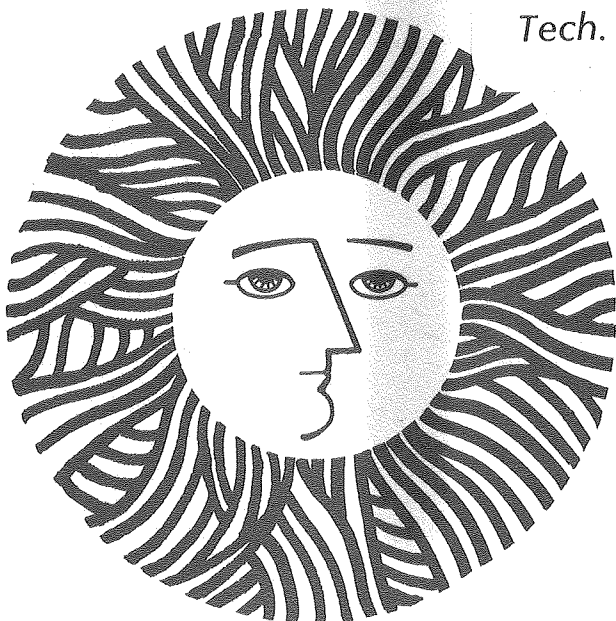
INVESTIGATION OF POSSIBLE METHODS FOR REMOVAL OF  
NITROGEN FROM COAL-DERIVED AND COAL-RELATED MATERIALS

Douglas D. Frey and Theodore Vermeulen  
(M.S. thesis)

September 1980

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Investigation of Possible Methods for Removal of Nitrogen  
from Coal-Derived and Coal-Related Materials

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Abstract

A preliminary study was conducted to determine the feasibility of removing nitrogen from hydrogenated coal products by oxidation. Solvent-refined coal, melt-treated coal, and nitrogen containing model-compounds were used as substrates. In addition, various zinc containing catalytic systems were screened for their hydrogenation and hydrocracking activity towards quinoline.

Results indicate that nitrogen can be removed from some of the model-compounds used. Both iron and cobalt salts effectively catalyzed the oxidation reaction. Very little nitrogen could be removed from the compounds that are the most representative of hydrogenated coal. In addition, very little nitrogen was removed from the hydrogenated coals themselves. None of the zinc salts tested in the hydrogenation portion of the study were effective in catalyzing the rate of hydrogenation of quinoline.

\* M. S. Thesis



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## I. Introduction

### A. Potential for Coal Utilization

The general public, various governmental agencies, and the scientific community are all vitally concerned with the need to develop viable alternative energy resources to replace dwindling world-wide oil supplies. Over the past decade, significant progress has been made in expanding research and development efforts into pilot plant and production-scale facilities in both coal hydroprocessing and other areas of coal processing technology. The production of synthetic fuels from coal now appears to be one of the most promising alternatives for early commercialization.

Coal is one of the world's most abundant fossil-energy resources. Current estimates indicate that coal reserves in the United States could supplant the use of oil and natural gas for the equivalent of 500 years (C1). In addition, coal has the potential of becoming a material of considerable economic importance to the United States by reducing payments for imported oil. In particular, there is a growing need for producing liquid products from coal for use as transportation fuels.

### B. Coal Composition and Origin

Coal is an extremely complicated polymeric material composed of carbon, hydrogen, oxygen, and to a lesser extent sulfur, nitrogen, and mineral matter. It is the fossilized remains of ancient plants and animals, especially of the carboniferous period of the paleozoic era nearly 400,000,000 years ago. Coal formation began when large masses of plant material, with the help of microorganisms, were transformed into peat and then buried underground by large-scale geological movement.

Later, through the little understood process of coalification, a chemical transformation took place which converted peat into lignite (or brown coal), bituminous coal, and finally into anthracite coal.

Several models for coal structure have been developed (W1, S1). Usually they represent coal as consisting of clusters of aromatic centers, connected by ether and alkyl bridges to form a high-molecular-weight material such as illustrated by the Shinn model (S1) in Figure 1. This makeup of coal is complicated further by inclusion in its pores of smaller molecules, which add to its overall heterogeneity without being part of the basic chemical structure (V1).

Comparison of the analysis of coals, crude oil, and gasoline (Table 1) shows that major chemical transformations must take place to produce useful products from coal. There must be a considerable reduction in molecular weight, an increase in the atomic H/C ratio, and effective removal of heteroatoms and ash, to produce either a synthetic crude oil, gasoline, or other chemical products.

The Shinn model suggests that coal can be converted into liquid products by a combination of breaking and capping aliphatic and ether linkages, and by hydrogenation and hydrocracking of the aromatic centers in coal. The resulting products would contain polyaromatic fragments suitable for subsequent upgrading by conventional hydrocarbon processing techniques.

The products of coal liquefaction contain a wide spectrum of aromatic, polyaromatic, and heterocyclic components. For this reason, it is usually convenient to characterize these products by giving their analysis in terms of their oil, asphaltene, and preasphaltene content. Oil is defined as the material exclusively soluble in cyclohexane. It

A MODEL OF SUB-BITUMINOUS COAL STRUCTURE (AFTER SHINN, BASED ON WORK DONE BY MOBIL RESEARCH CO.)

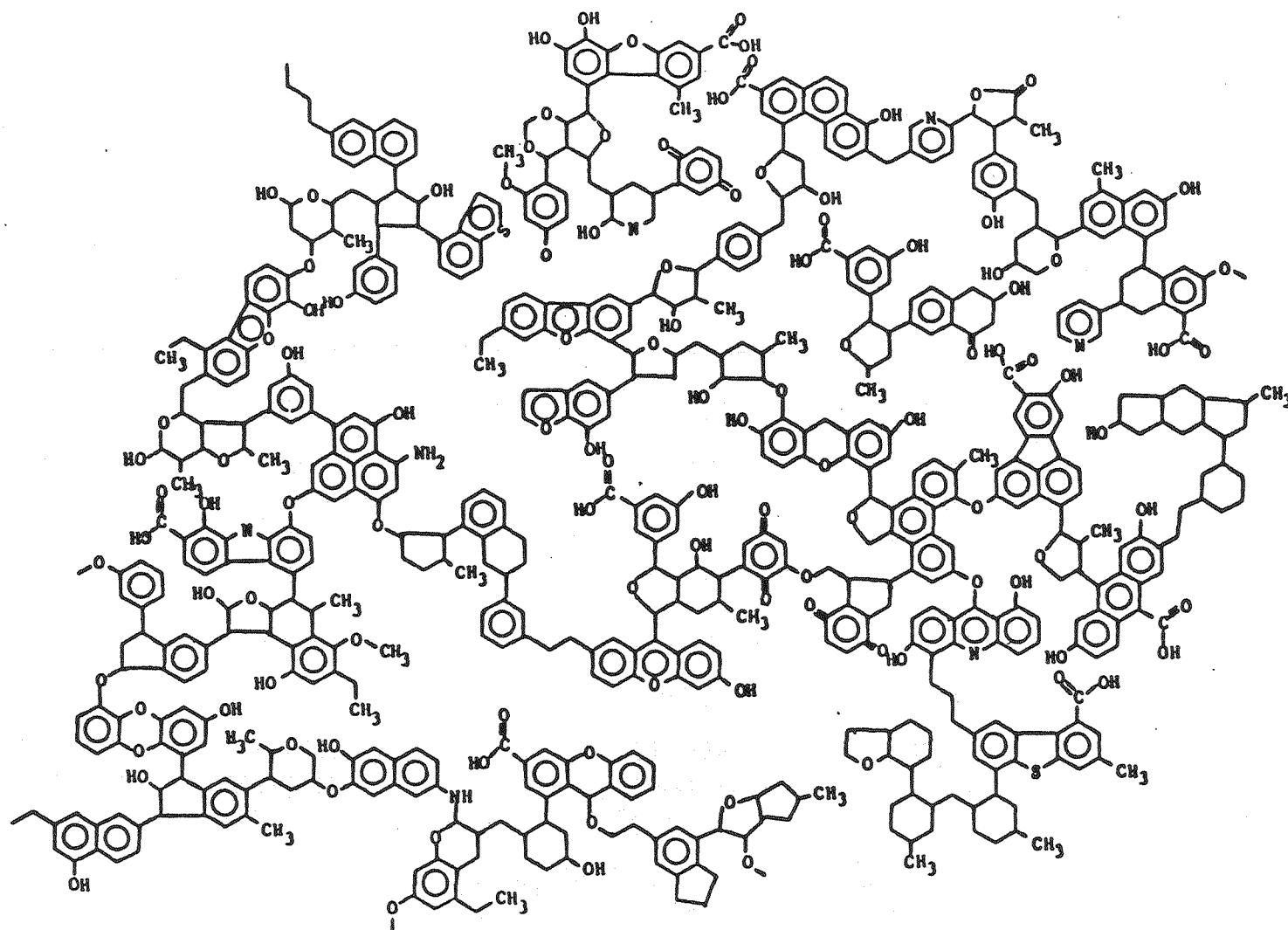


Fig. 1.

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Table I. Comparative Analyses of Coals, Crude Oil and Gasoline. ( wt%, MAF)

	<u>Anthracite Coal</u>	<u>Medium Volatile Bit. Coal</u>	<u>High Volatile Bit. Coal</u>	<u>Crude Oil</u>	<u>Gasoline</u>
C	93.7	88.4	84.5	83-87	86
H	2.4	5.0	5.6	11-14	14
O	2.4	4.1	7.0	-	-
N	0.9	1.7	1.6	0.2	-
S	0.6	0.8	1.3	1.0	-
H/C*	0.31	0.67	0.79	1.76	1.94
ash	----- (up to 15%) -----			-	-

\*  
Atomic H/C ratio

is the desired product from coal liquefaction, and has the highest H/C ratio. Asphaltene, defined as material which is toluene-soluble but not cyclohexane-soluble, is intermediate in terms of molecular weight and H/C ratio. Preasphaltene, defined as material soluble in pyridine but not in toluene, tends to have the highest average molecular weight, the lowest H/C ratio, and the highest heteroatom content.

### C. Coal Liquefaction

The proposed processes for conversion of coal into synthesis products can be divided into two main types: direct conversion, and indirect conversion.

Indirect conversion involves producing synthesis gas from coal, which is then catalytically converted to liquid products at moderate temperature and relatively high pressure. Due to poor process economics, indirect conversion has not been practiced on a large scale since World War II, except for a plant ("Sasol") in South Africa. A significant recent improvement has been to use shape-selective zeolite catalysts to convert methanol produced from synthesis gas into gasoline, avoiding the formation of lower- and higher-molecular-weight products.

Direct conversion processes convert coal into liquid products without producing gas as an intermediate. Among the processes considered for commercialization are pyrolysis, hydrolysis, and various catalytic hydrogenation processes. Pyrolysis and hydrolysis depend upon thermal breaking of bonds in coal to produce lower-molecular-weight products, and generally yield large amounts of char and gas products as well. In contrast, catalytic hydrogenation processes aim to achieve high yields of desired liquid products at moderate reaction conditions through the use of selected catalytic materials.

In a typical catalytic hydrogenation process, ground coal is slurried with a recycle oil, mixed with hydrogen, and introduced into a fluidized-bed catalytic reactor (D1). The reactor effluent is fractionated, and the liquefaction products are upgraded by conventional hydrocarbon-processing methods.

The use of metal halides for coal conversion has been investigated by many workers. The most recent work has emphasized the use of metal chlorides, particularly zinc chloride, as liquid-phase catalysts for coal conversion. Shinn (S1) has achieved nearly complete conversion of Wyodak coal to pyridine-soluble material using  $\text{ZnCl}_2$  diluted with methanol at 275°C and 800 psi. Other work on model-compounds (M1) has suggested that the mechanism for coal conversion using  $\text{ZnCl}_2$  includes the selective breaking of ether linkages.

#### D. The Oxidation of Hydrocarbons, Coal, and Coal-Related Materials

A portion of this study will involve investigation of the effects of oxidation on various organic compounds and mixtures. A brief review of this subject is therefore in order.

##### 1. Hydrocarbon Oxidation

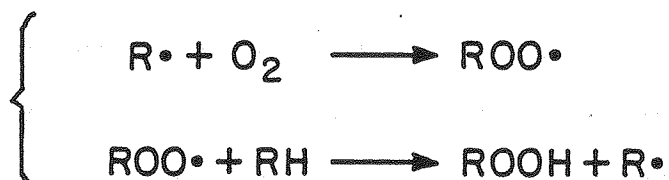
Low-temperature oxidation of pure hydrocarbons has been of considerable interest to both the scientific community and to the chemical industry. The subject has been investigated under a variety of conditions, and the effects of solvent polarity, catalysts, pressure, initiators, inhibitors, and substituent functional groups have all been studied (B1, B2, C2, G1, V2).

In Figure 2, the major steps involved in the low-temperature oxidation of paraffins are shown. A primary product of hydrocarbon oxidation is a hydroperoxide. At low temperatures (100°C-200°C), these

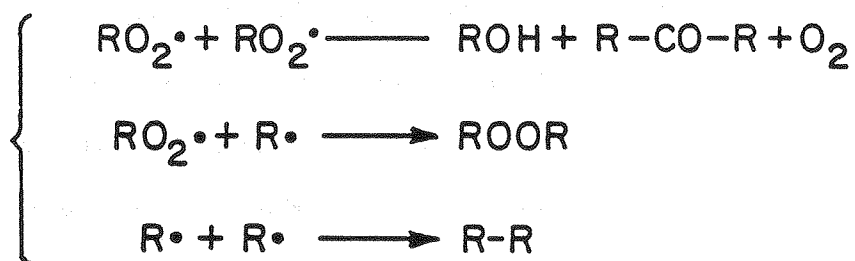
Initiation



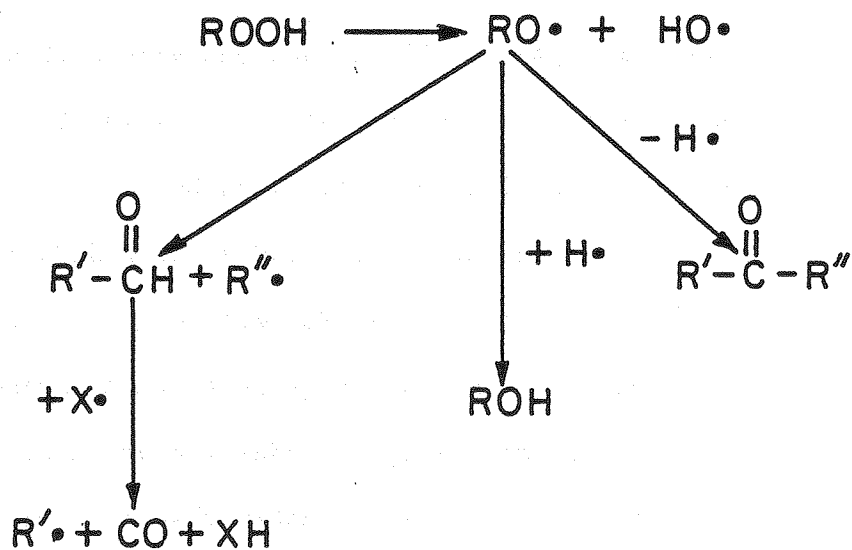
Propagation



Termination



Branching



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Fig. 2 Paraffin Oxidation

hydroperoxides decompose to form alcohols, ketones, and aldehydes (B3). At higher temperatures, the role of hydroperoxides is taken by aldehydes (C3). Secondary alcohols, the predominate alcohol product from paraffin oxidation, react to form ketones and these in turn react to form more highly oxidized products. By an alternate path, hydroperoxides can also form alcohols, carbon monoxide, and products with fewer carbon atoms than the initial hydrocarbon (B4). The smaller fragments may be either hydrocarbons or oxygenated products depending on the availability of oxygen in the system.

The major effect of aromatic nuclei, heteroatoms, and other functional groups appears to be on where oxidation takes place, through the effect on carbon-hydrogen bond strength (W2). Hydrogen atom abstraction occurs most easily at positions alpha to unsaturated groups due to the resonance stabilization of the resulting radical (S2). For this reason, allylic and benzylic carbon atoms are the most susceptible towards oxidation, followed by tertiary carbon, secondary carbon, and finally, primary carbon.

Many experimental studies on hydrocarbon oxidation have been conducted over the past several decades. To simplify the kinetic studies, self-initiation is usually disengaged from the remainder of the kinetic scheme by the addition of an initiator which provides free radicals at a rate much faster than the competing thermal initiation. This requires a fairly low temperature so that spontaneous autoignition processes are slow. In addition, the conversion is limited to a few percent so that degenerate branching processes caused by the accumulation of peroxides remain negligible. Under these conditions, oxidation is found to be first-order in substrate concentration, zero-



order in oxygen partial pressure, and proportional to the square root of the rate of initiation (V2).

## 2. The Oxidation of Coal and Coal-Related Materials

The oxidation of coal has been a subject of intense interest over the last fifty years. Many oxidants have been used, including potassium permanganate (B5), nitric acid (K1), hydrogen peroxide (C1), molecular oxygen (M2), ozone (K2), and potassium dichromate (H1). These studies have yielded valuable information concerning coal structure (K3), on the possibility of producing useful chemicals from coal (E1), on the mechanism for the low-temperature autoignition of coal (M2), and on the possibility of oxidative depolymerization of coal (H2).

All coals other than anthracites are so sensitive to oxidation that even short exposure to oxygen causes significant changes in many of their physical and chemical properties. The initial stages of oxidation are characterized by chemisorption of oxygen at surface sites, and the formation of acid, hydroxyl, and perhydroxyl functional groups (J1).

Above 70°C, the thermal instability of hydroperoxides modifies the oxidation reaction. Oxidation rates are now high enough to be controlled by mass transfer to the interior portions of the coal particles (B6). At about 150°C, the coal macromolecules begin to decompose to form alkali-soluble humic acids. These oxidation intermediates appear to be stable up to temperatures of about 250°C, where they are further oxidized to gaseous products and lower-molecular-weight products. Oxidants other than molecular oxygen attack coal in a similar manner but somewhat more indiscriminately.

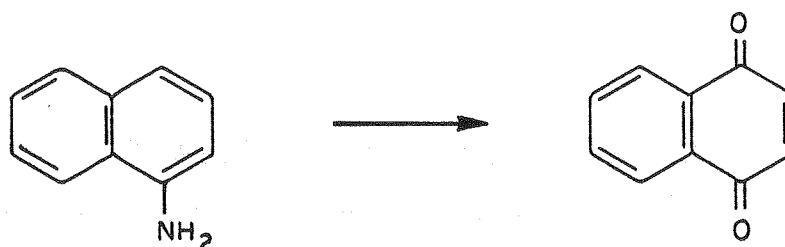
Several uses for oxidation in coal processing have been suggested. One of the most interesting recent developments involves using selective oxidation to break aliphatic and ether linkages in coal (H2). For example, aliphatic chains between aromatic centers should be easily oxidized to carboxylic acid pairs while alkyl ethers can be oxidized to esters which could be hydrolyzed to acids and alcohols. Recent work in this area shows that mild oxidation of extracted coal with subsequent base hydrolysis produces lower-molecular-weight fragments and incorporates significant amounts of oxygen. Thus, selective oxidation of breakable bonds in coal may be difficult to achieve without concurrent oxidation of the more reactive hydroaromatic centers and subsequent loss of coal heating value.

Second-stage liquefaction of solvent-refined coal by controlled low-temperature air oxidation in quinoline has also been reported (H3). In that study, solvent-refined coal was oxidized with molecular oxygen and then thermally stressed to induce hydroperoxide decomposition, giving significant yields of low-molecular-weight materials.

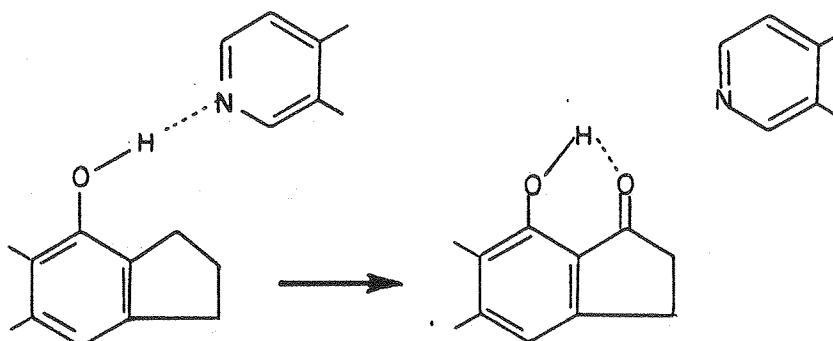
Oxidation has also been proposed as a means for producing commercially important chemicals from coal. The most feasible process would probably involve use of oxygen in an aqueous alkaline medium to produce benzene carboxylic acids. Kamiya's (K4) work on bituminous coals showed an overall yield of 26% for this conversion. Eisenberg (E1) obtained similar conversions from Western Kentucky coal char.

The degradative oxidation of a bitumen derived from Athabaskan tar has been studied recently by Moschepedes (M3, M4, M5). In these studies, bitumen dissolved in a solvent was exposed to oxygen at moderate temperatures (150°-250°C), both with and without soluble

transition-metal catalysts. Oxidation renders the bitumen less soluble in organic solvents, and alters the elemental analysis of the solvent-extracted fractions. The data seem to indicate that a combination of polymerization and increased polarity reduces the solubility. Also, the N/C and S/C ratios are decreased in the cyclohexane-s-luble (oils) fraction of the products, suggesting that polar centers in the bitumen are the most susceptible toward oxidation. The net reduction in nitrogen led the investigators to propose reactions such as



This reaction is known to occur in the case of oxidation using lead tetraacetate (P1). Homogeneous oxidation catalysts not only accelerate bitumen oxidation, but also modify the chemical nature of the oxidation products. Hence, these catalysts would appear to maintain their integrity effectively, unlike homogeneous hydrogenation catalysts which under similar conditions may easily be stripped of their activating ligands (H4). Finally, Moschepedes postulated that since resins are responsible for the peptization of asphaltenes, the creation of polar groups by oxidation would promote intramolecular hydrogen bonding at the expense of intermolecular hydrogen bonding, and aid in peptization of asphaltenes. For example, hydrogen bonding between basic nitrogen and phenolic hydrogen could be replaced by intramolecular hydrogen bonding as shown below.



#### E. The Nature of Nitrogen in Coal and Coal-Related Materials

Coal usually contains about 1 to 2 wt-% of nitrogen while the original plant material from which it is derived contains about 0.1%. This relation suggests that a large part of the original material has been destroyed, and that the nitrogen-containing molecules are highly stable.

Coal conversion under mild conditions yields products which are still high in nitrogen. As shown by the data in Table II from work done by Tanner (T1), the products from the  $\text{ZnCl}_2$  catalyzed hydrogenation of solvent-refined coal under the listed conditions show very little net hydrodenitrogenation. Instead, there appears to be a pronounced segregation of nitrogen into the preasphaltene fraction.

These data seem to support Sternberg's theory that preasphaltenes are composed of acid-base pairs (S3). In Sternberg's work, preasphaltenes were separated into an acid fraction and a basic fraction using dry hydrogen chloride gas. The acidic fraction contained oxygen as phenolic groups, and nitrogen has pyrrole groups. The basic fraction contained ring oxygen and basic nitrogen. Sternberg postulated

Table II.  $\text{ZnCl}_2$ -Catalyzed Hydrogenation of  
Solvent-Refined Coal (300°C, 2000  
psig, 90 min.) from Tanner (T1).

SRC feed formula

$\text{CH}_{.77}\text{N}_{.022}\text{S}_{.023}$

	Cyclohexane Filtrate Formula and <u>Yield (wt-%, MAF)</u>	Residue Formula and <u>Yield (wt-%, MAF)</u>
SRC hydrogenated at 300°C, 200 psig, 90 min., no catalyst	$\text{CH}_{.9}\text{N}_{.014}\text{S}_{.002}$ (15.1)	$\text{CH}_{.80}\text{N}_{.022}\text{S}_{.0023}$ (84.9)
SRC hydrogenated at 300°C, 2000 psig, 90 min., catalyzed by $\text{ZnCl}_2$	$\text{CH}_{1.06}\text{N}_{.0013}\text{S}_{.0016}$ (35.4)	$\text{CH}_{.95}\text{N}_{.027}\text{S}_{.0031}$ (64.6)

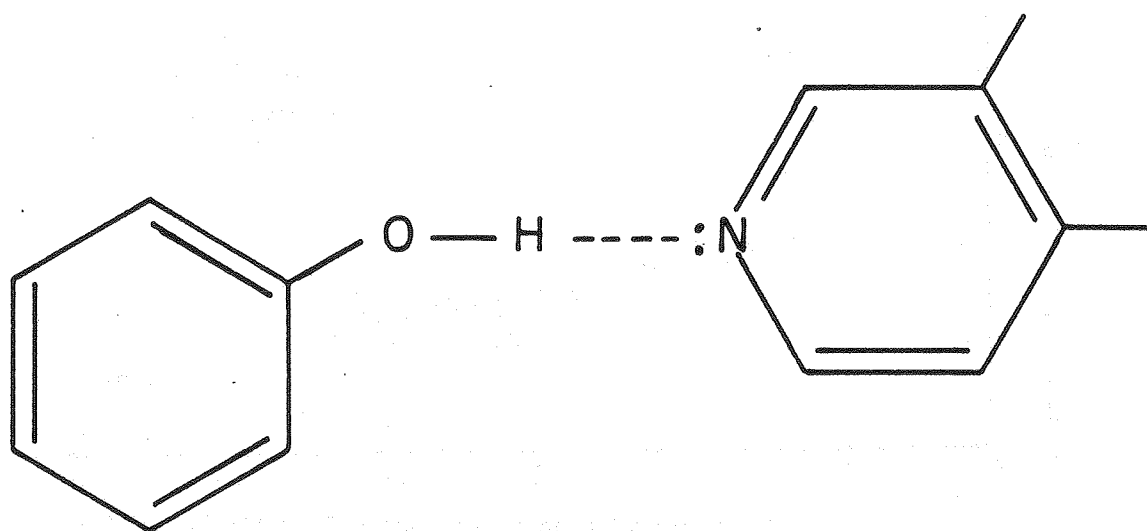
that complex formation occurs by hydrogen bonding between acidic phenol and basic nitrogen groups (Figure 3).

Methods for removal of nitrogen from organic materials include hydrogenation, oxidation, acid extraction, and diazotization. Hydrogenation appears to be most straight-forward, and has been the subject of extensive investigation (for example K5, K6). Nitrogen-containing rings in model-compounds appear to be hydrogenated selectively due to the higher electronegativity of the nitrogen atom with its unshared pair of electrons (K6). However, hydrodenitrogenation of model-compounds seems to occur only by complete saturation of the aromatic ring because of the resonance between it and the unshared electrons of the nitrogen. For this reason, hydrodenitrogenation of coal is especially expensive in terms of hydrogen consumption. The relation between hydrogen usage and nitrogen removal is illustrated in Figure 4 for hydroliquefaction of several coals (W3).

#### F. Objectives of the Present Research

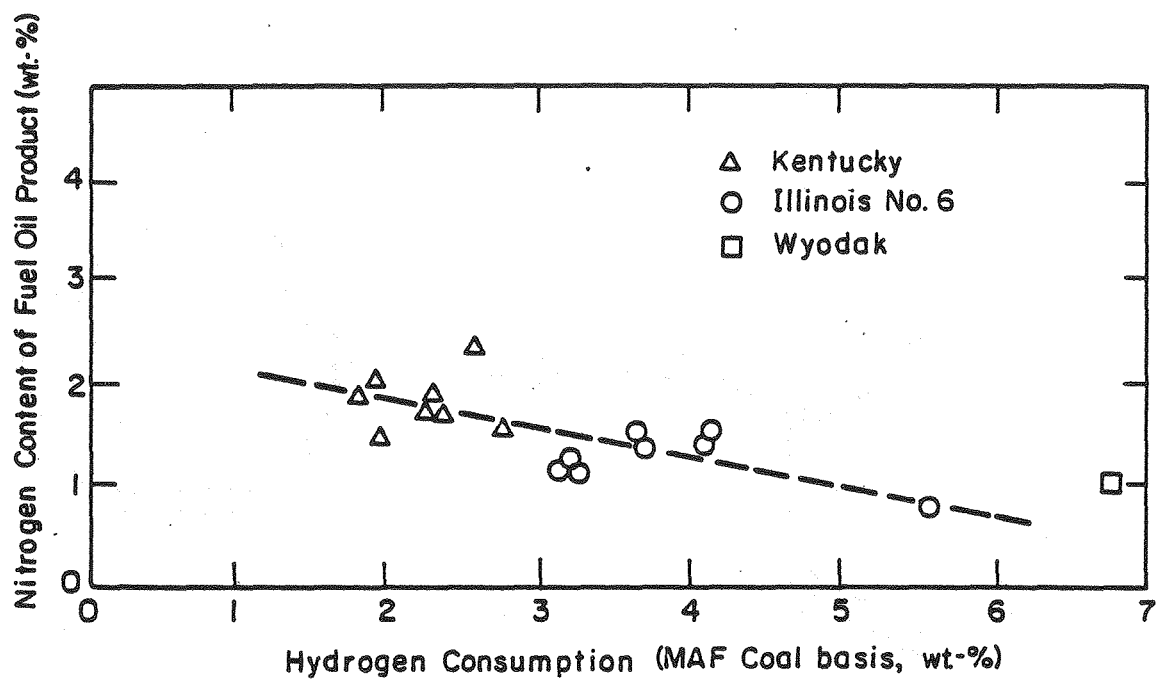
The objective of this research is to investigate reaction conditions under which nitrogen can be removed from coal and coal-related materials. A further objective is to investigate the form and nature of nitrogen in coal products, particularly preasphaltenes.

Two main reasons justify this interest in coal nitrogen. First, when fuels containing nitrogen are burned, nitrogen oxides are formed which then enter the air as a pollutant. Second, since preasphaltenes appear to consist of acid-base pairs involving nitrogen, the selective removal of this nitrogen should serve to break up the preasphaltene molecules and form the more desirable oils and asphaltenes. As previously indicated, current hydrodenitrogenation techniques are expensive



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Fig. 3 Acid-Base Complexing in Preasphaltenes.



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Fig. 4. Hydrogen Required to Reduce Coal Nitrogen, from Wolk (W3).



in terms of hydrogen consumption, and must take place under conditions of high temperature and pressure. This fact leads to the possibility that a better method for nitrogen removal may be to hydrogenate heterocyclic rings in coal and then chemically to remove nitrogen in a subsequent processing step.

One plausible choice for subsequent processing would be mild controlled oxidation. As previously noted, Moschepedes (M2) has reported nitrogen removal from bitumen by oxidation. In addition, amine oxidation has been studied extensively in both the liquid and gas phase. Cullis (C5) has studied the oxidation of low-molecular-weight amines and noted a substantial production of ammonia and other nitrogen containing gases. Kovtun (K7, K8) has similarly studied higher-molecular-weight amines. The basic objective of this research is to perform a preliminary and exploratory study on the feasibility of oxydenitrogenation of hydrogenated coal.

Another objective of this research will be to investigate the hydrogenation, hydrocracking, and hydrodenitrogenation activity of various zinc-containing catalytic systems toward nitrogen-containing model compounds. Several investigators (S1, Z1) have had considerable success in the use of zinc compounds as catalysts for the conversion of coal to soluble materials under mild conditions. These zinc compounds have the potential of being used either for direct hydrodenitrogenation, or for preliminary hydrogenation prior to a subsequent processing step.

Finally, the use of low-temperature oxidation may have other beneficial effects in coal processing. For example, oxidation has the potential of cleaving certain bonds in coal to assist in liquefaction. In addition, as previously discussed, oxidation may increase solubilization by introducing intramolecular hydrogen bonding.

## II. Experimental Apparatus and Procedure

### A. Materials Used

The materials used in this study are listed in Table III. All of the materials were used as received, except for the following:

1) Solvent-refined coal (SRC) was obtained from the Pittsburgh and Midway Coal Mining Company in sealed five-gallon cans. The SRC was dried overnight in a nitrogen-purged vacuum oven at 105°C, and then ground in a ball mill inside a nitrogen-purged glove box. The ground material was sieved, and the -28+100 mesh fraction was saved and stored under nitrogen in tinned friction-lid cans. The analysis of the SRC is shown in Table IV.

2) Coal hydrogenated under mild conditions using massive amounts of  $\text{ZnCl}_2$  as a liquid phase catalyst was obtained from co-workers at the University of California. The melt-treated coal (MTC) was dried overnight in a nitrogen-purged vacuum oven at 105°C, sealed in air-tight vials, and stored in a desiccator. Two types of MTC with different H/C ratios were used. The MTC with the highest H/C ratio was hydrogenated using zinc metal as a co-catalyst in the zinc chloride melt. The analysis of these materials is given in Table IV.

3) Benzylamine and 1,2,3,4-tetrahydroisoquinoline were distilled in an all-borosilicate-glass distillation apparatus at reduced pressure. They were then stored at 5°C under nitrogen in brown-glass bottles.

4) Quinoline was extracted with solid potassium hydroxide for 24 hours immediately prior to use, to ensure the absence of dissolved water.

Several other materials were prepared in the following ways. The double iodide of potassium and mercury was prepared by adding a

Table III. Sources and Purities of Chemicals Used

Material	Source	Grade	Min. Purity (%)
Acetic Acid	Mallinkrodt	Reagent	98
Acetic Anhydride	Mallinkrodt	Reagent	98
Aniline Hydrochloride	Matheson, Coleman, and Bell	-	-
Azobisisobutyro- nitrile	Aldrich	Aldrich Analyzed	-
Benzaldehyde	Matheson, Coleman,	-	-
Benzamide	Eastman	-	-
Benzene	Matheson, Coleman, and Bell	Spectro- quality	-
Benzylamine	Aldrich	Aldrich Analyzed	*
Caprylic Acid	Matheson, Coleman, and Bell	Reagent	-
Chlorobenzene	Aldrich	Aldrich Analyzed	-
Co(acac) <sub>3</sub>	Alfa Inorganics	-	-
Cyclohexane	Mallinckrodt	Reagent	-
2,3 cyclohexeno- pyridine	Aldrich	Aldrich Analyzed	-
m-Dichlorobenzene	Aldrich	Aldrich Analyzed	98
Fe(acac) <sub>3</sub>	Alfa Inorganics	-	-
Ferric Sulfate	Matheson, Coleman, and Bell	Reagent	-
Hydrochloric Acid	Mallinckrodt	-	30
Hydrogen	Liquid Carbonic	-	99.999
Hydrogen Peroxide	Mallinckrodt	-	30
Mercuric Chloride	Baker and Adamson	Reagent	-
Methanol	Mallinckrodt	Reagent	-
Molecular Sieves	Linde	-	-
Nitrogen	Liquid Carbonic	-	99.999
Ni(acac) <sub>2</sub>	Alfa Inorganics	-	-
Oxygen	Pacific Oxygen	-	99.999
Phenylenediamine Dihydrochloride	Eastman	-	-

Table III. Continued

Material	Source	Grade	Min. Purity (%)
Phenylether	Eastman	-	98
Phenoltheinlene	Mallinckrodt	Reagent	-
Potassium Iodide	Baker and Adamson	-	99.8
n-propylaniline	Eastman	-	-
n-propylbenzene	Aldrich	Aldrich Analyzed	98
Pyridine	Mallinckrodt	Reagent	-
Quinoline	Aldrich	Aldrich Analyzed	96*
Sodium Chloride	Mallinckrodt	-	98
Sodium Hydroxide	Mallinckrodt	-	-
1,2,3,4 Tetrahydro isoquinoline	Aldrich	Aldrich Analyzed	98*
1,2,3,4 Tetrahydro- quinoline	Aldrich	Aldrich Analyzed	97
Tetralin	Eastman	Practical	-
Toluene	Mallinckrodt	Reagent	-
1,2,4 Trichloro- benzene	Eastman	Practical	-
Zinc Benzoate	Chemical Indust. Magazine	-	-
Zinc Chloride	Matheson, Coleman, and Bell	Reagent	98
Zinc Phenolate	E de Haen Chem. Works	-	-
Zinc Salicylate	Eilmer and Amend	-	-
Zinc Sulfate	Mallinckrodt	Reagent	98

\* Repurified as described in text

Table IV. Analysis of Hydrogenated Coals

Analysis (wt-%, MF)								
<u>Material</u>	<u>%C</u>	<u>%H</u>	<u>%N</u>	<u>% O+S</u>	<u>ash</u>	<u>H/C</u>	<u>Toluene</u>	<u>Pyridine</u>
SRC	87.11	5.61	2.25	5.03	-	.77	65	100
MTC 1	70.72	5.94	0.94	8.54	11.3	1.01	31	88
MTC 2	67.29	6.48	0.75	3.88	14.0	1.16	47	100

saturated solution of mercuric chloride to 50 gm of potassium iodide in 35 ml of water until a red precipitate formed. Next, 400 ml of 36% NaOH was added. The mixture was allowed to settle, after which the liquid phase was decanted and stored in a polyethylene bottle.

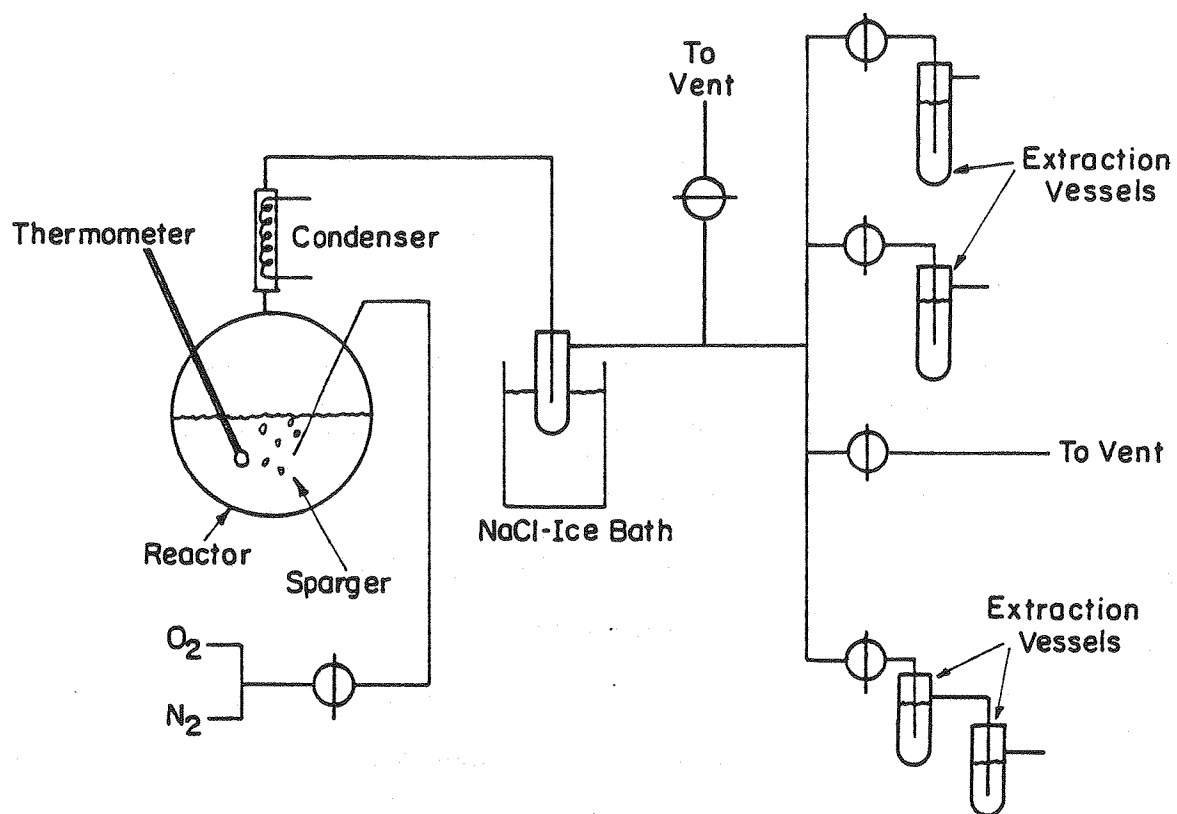
An absorbing solution for nitrogen oxide gas was prepared by dissolving 5 gm of sulfanilic acid in almost one liter of nitrite-free water (prepared by distilling deionized water to which one crystal each of  $\text{Ba}(\text{OH})_2$  and  $\text{KMnO}_4$  had been added). Next, 50 ml of glacial acetic acid was added along with 50 ml of a 0.1% solution of phenylenediamine dihydrochloride, and the total volume was brought to one liter. This reagent was kept tightly stoppered in a dark bottle.

Zinc caprylate was prepared by adding a zinc sulfate solution to an equivalent amount of sodium caprylate (prepared by neutralizing caprylic acid with sodium hydroxide to the phenolphthalein endpoint). The crude product was repeatedly washed with distilled water, and then dried in a nitrogen-purged vacuum oven at  $105^\circ\text{C}$ . The material obtained, compared with theory for pure zinc caprylate, had an elemental analysis of Zn, 18.0% (18.2%); C, 53.6% (54.0%); H, 8.46% (8.6%) and O, 19.9% (19.2%).

#### B. Apparatus

Oxidation experiments at atmospheric pressure were performed in the apparatus shown in Figure 5. The reactor consisted of a round-bottom flask equipped with a fritted glass sparger, reflux condensor, and stirrer. The vent gas from the reactor could be continuously extracted by passing it through an assembly of fritted glass spargers immersed in appropriate absorbing solutions.

Oxidation and hydrogenation experiments at high pressure were performed in a glass-lined 600 ml stainless steel autoclave manufactured



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Fig. 5 Experimental Apparatus for Atmospheric Pressure Oxidation

by Parr Instrument Co., Moline Illinois (Figure 6). The autoclave was equipped with a 2000 psig rupture disk. When corrosive conditions were encountered, a Hastelloy B autoclave of similar design was used. Agitation was accomplished with a direct-drive stirrer using self-sealing packing glands. Heat was supplied by a 780-watt mantle, and temperature was controlled with a solid-state potentiometric system utilizing an iron-constantin thermocouple. An internal cooling loop was controlled through a solenoid valve. A back check valve on the gas feed lines prevented any gases from backing up into the gas feed cylinders.

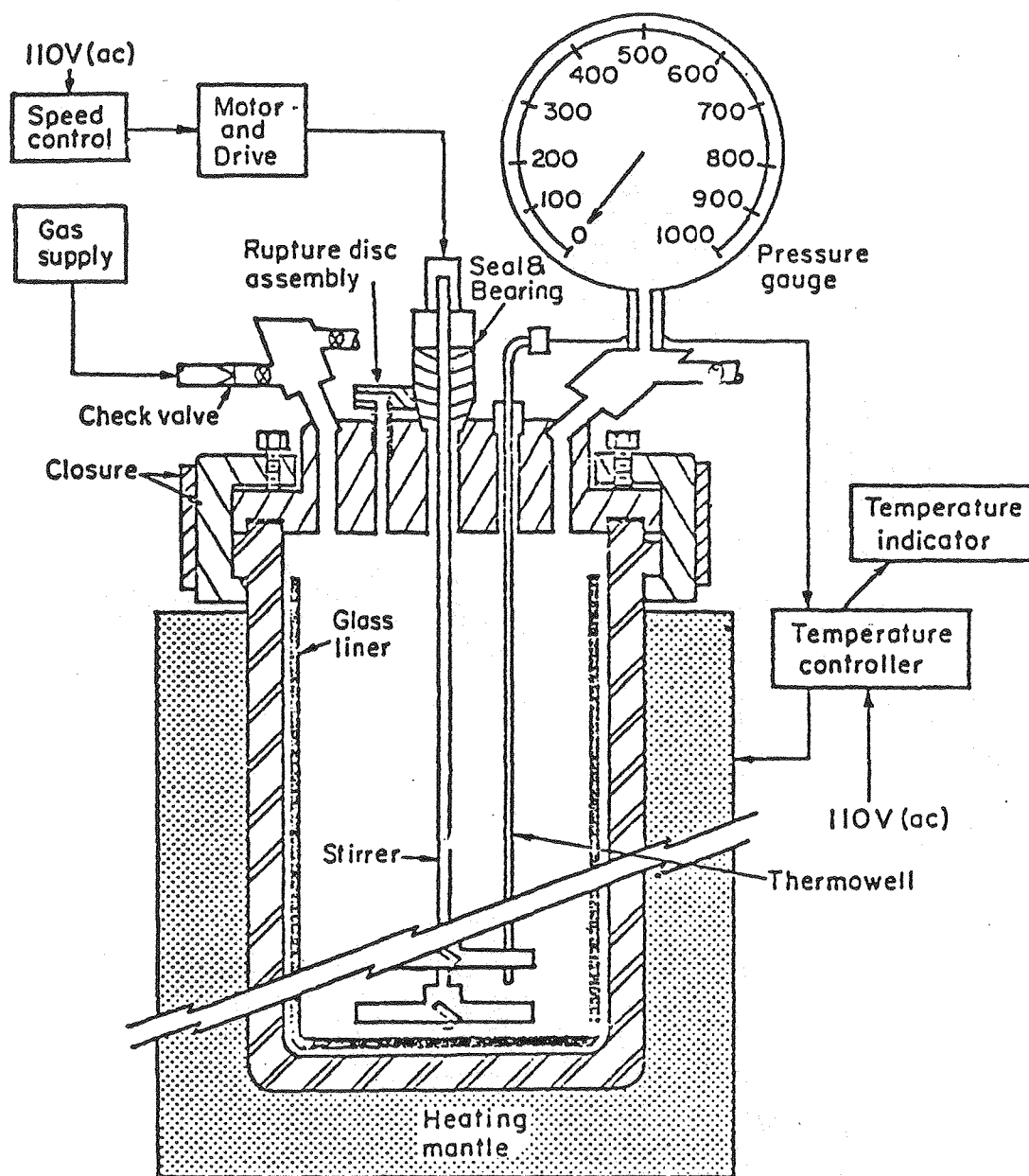
### C. Procedure

#### 1. Model-Compound Oxidation at Atmospheric Pressure

The general procedure used for the model-compound oxidation experiments at atmospheric pressure is shown in Figure 7. The system was first purged with nitrogen, the vent gases being discharged to the atmosphere. After the purging is completed, the substrate, solvent, and any additives were introduced into the reactor at ambient temperature. The reactor was then brought to the desired temperature by means of a Glas-col heater. During the heatup, dry nitrogen was continually sparged at low flowrate into the reactor to remove any dissolved gases. When the desired temperature was reached, the nitrogen flow was stopped, and oxygen flow was started.

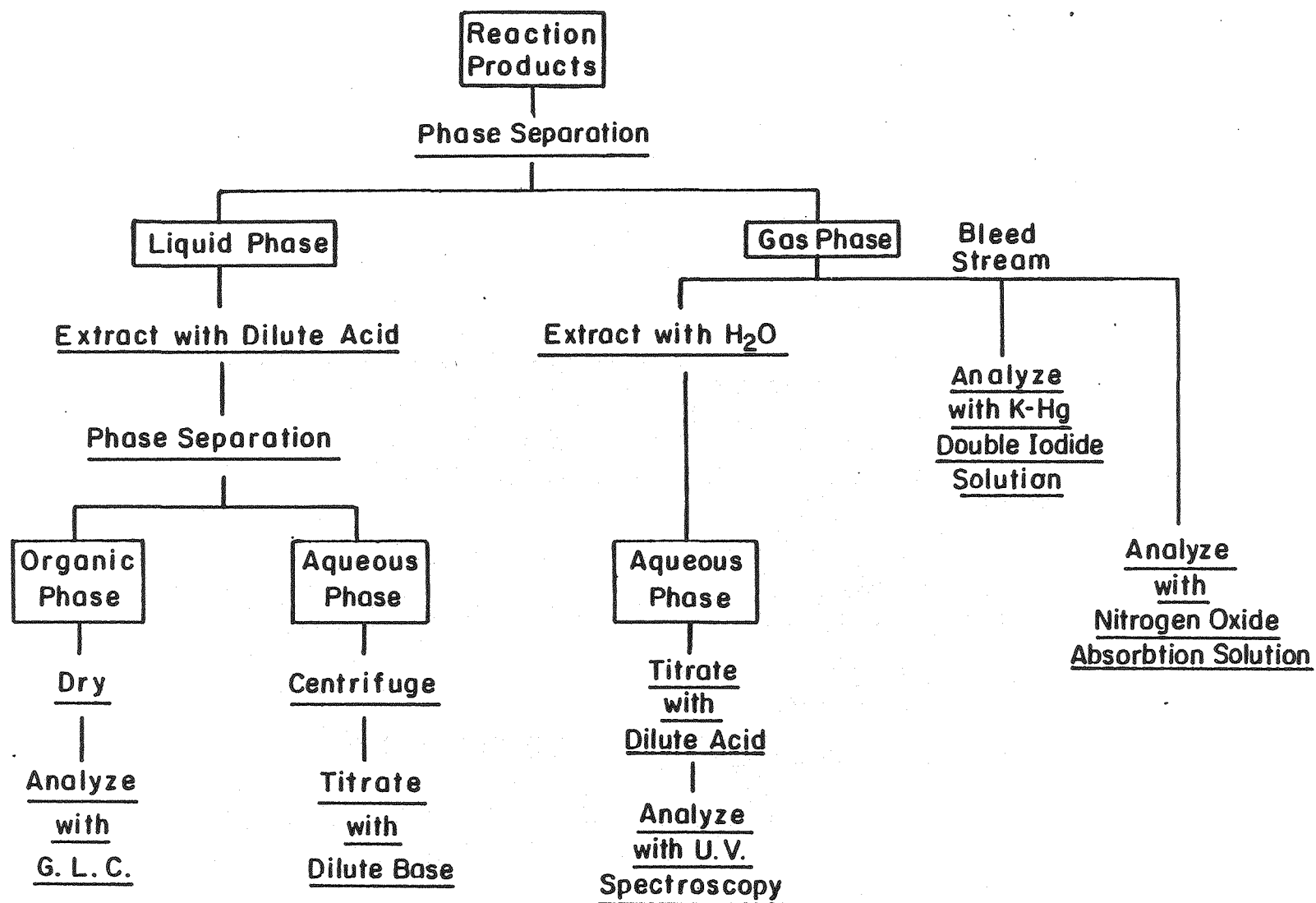
The reactor vent gas was then directed into the absorbing solutions. The vent gas first passed through an overhead water-cooled condenser, where solvent was condensed and returned to the reactor. The gas next passed through a cold trap maintained at  $-10^{\circ}\text{C}$ , and finally passed into water through two fritted-glass bubblers connected in series. In addition, the vent gases were also sampled for ammonia and nitrogen





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Fig. 6. Parr Autoclave



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Fig. 7 Procedure for the Workup of the Products of the Model-Compound Oxidation Experiments

oxides by passing a small bleed stream through two absorbing solutions connected in parallel, consisting of the potassium-mercury double iodide and the sulfanilic acid-phenylenediamine solution.

The vent gas extract was then titrated for total base with a standard solution of hydrochloric acid; sometimes using a 0.1% alcoholic solution of methyl red as an indicator, but more often using a Coleman Model 38 pH meter and terminating the titration at pH 5. The titer obtained was assumed to consist of ammonia plus any unreacted amine removed from the reactor. The latter was determined by measuring the absorbance of the aqueous extract with a Varian-Cary model 219 Ultra-violet Spectrophotometer, after first adjusting the extract's pH to a value for which the amine's extinction coefficient had previously been measured.

After the reaction was completed, the reactor was rapidly cooled to ambient temperature. A small quantity, usually 1-2 gm, of the reactor contents was transferred into a tared flask and weighed. The contents of the flask was then quantitatively transferred to a separatory funnel where it was extracted with a precisely determined volume of a standard solution of hydrochloric acid. The aqueous phase of the extract was then quantitatively transferred into another container, and, after first centrifuging to remove colloiddally dispersed solvent, was titrated with a standard solution of sodium hydroxide. The unreacted amine per unit weight of residual reactor contents could then be determined by difference. The organic phase of the extract was dried with 5 Å molecular sieve, and then analyzed by gas chromatography as described below.

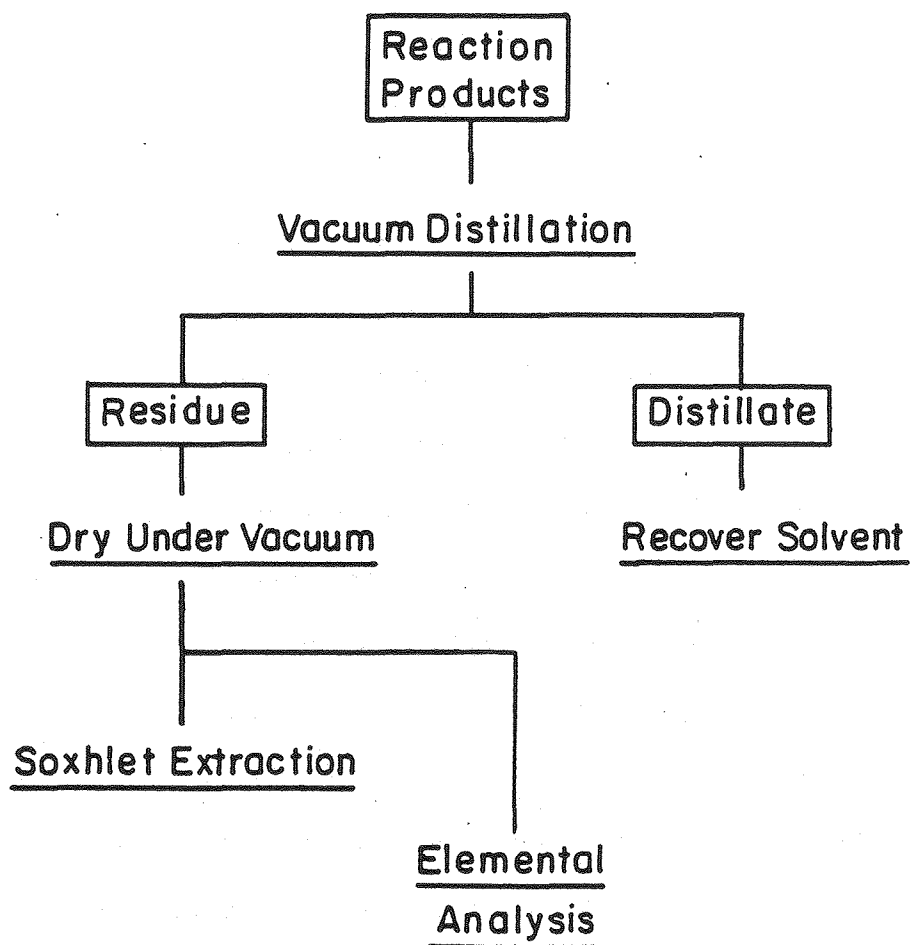
## 2. Hydrogenated Coal Oxidation at Atmospheric Pressure

When SRC or MTC was used as the substrate for the experiments, the procedure illustrated in Figure 8 was used. In this procedure, the reactor was connected to a small distillation apparatus immediately after the reaction was completed. The solvent was then removed under vacuum. The residue remaining in the reactor was removed, and dried for 48 hours at 150°C under 40 mm Hg of nitrogen in a vacuum oven. The dried and ground product was then Soxhlet-extracted. In addition, a small sample of the product was submitted to the Microanalytical Laboratory for elemental analysis.

For reactions in aqueous media, the substrate was first wet with about 25% by weight of water. The oxidant was then added, along with any other additives, and the slurry was heated to reaction temperature. After the reaction was completed, the contents of the reactor were removed and filtered through a medium-frit sintered glass filter. The filter cake was washed with 500 ml of deionized water, and then dried overnight at 105°C in a vacuum oven. The product was then Soxhlet-extracted, and a sample of the product was submitted for elemental analysis.

## 3. Model-Compound Oxidation at High Pressure

A Parr reactor was used for the high-pressure oxidation experiments conducted on model-compounds. In these experiments, the substrate, solvent, and any additives were added to a glass liner which was immediately inserted into a preheated Parr reactor. The bomb was sealed and purged with nitrogen, heated to the desired temperature, and then pressurized with oxygen. After the reaction was completed, the bomb was cooled to ambient temperature by cautiously applying a water-soaked



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Fig. 8. Procedure for the Workup of the Products of the Hydrogenated Coal Oxidation Experiments.

sponge. The gases in the bomb were discharged into a gas-absorber vessel. The liquid products remaining in the reactor, as well as the reactor gas extract, were analyzed as described in section III.C.1.

#### 4. Quinoline Hydrogenation

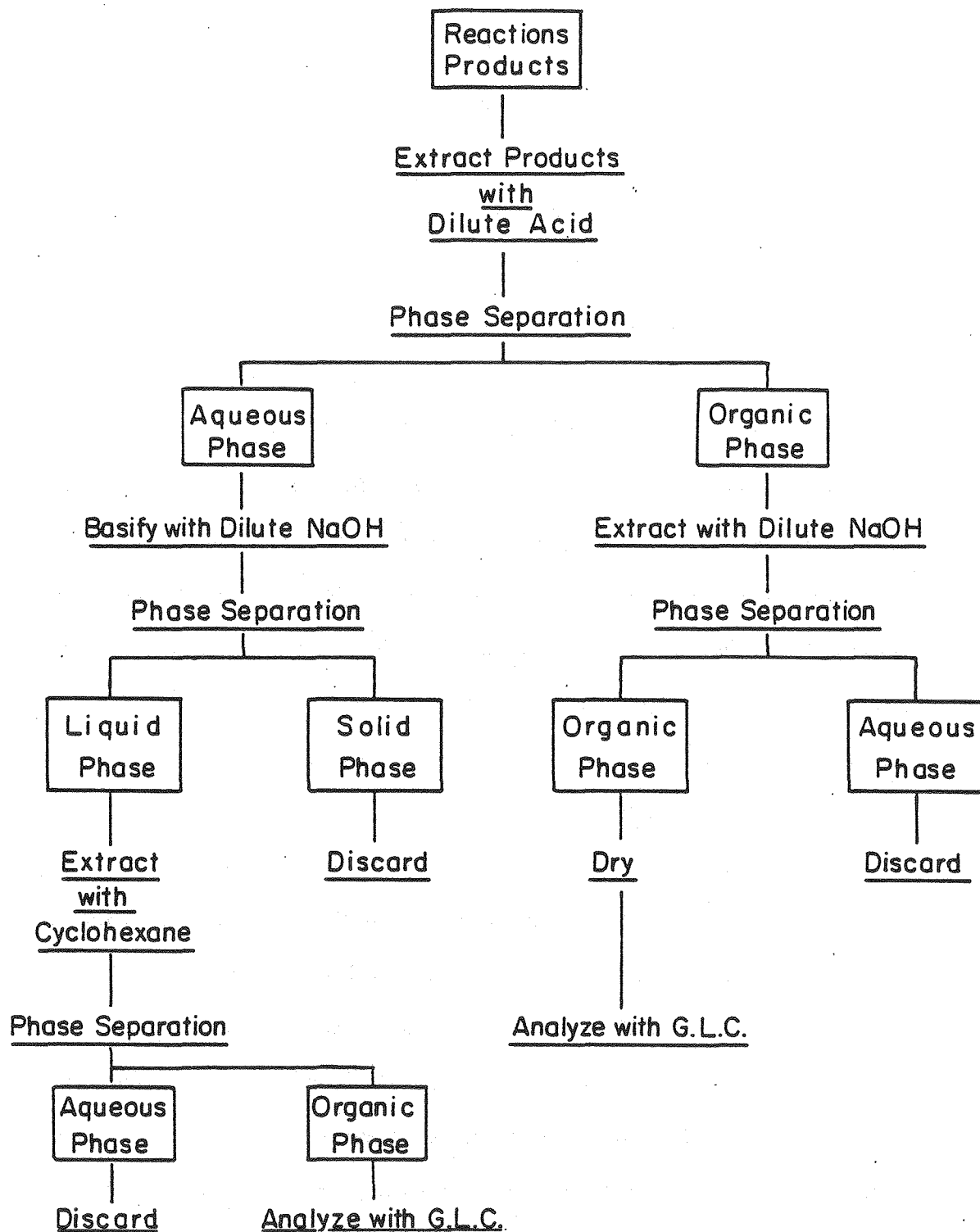
The procedure for the workup of the products of the quinoline hydrogenation experiments is shown in Figure 9. In these experiments, the solvent and any additives were preheated in a Parr reactor, to which the substrate was added. The reactor was then sealed, purged, heated to 150°C, and pressurized with hydrogen to a pressure which would yield the desired hydrogen partial pressure at the reaction temperature. The reactor was then heated to the desired temperature. When the reaction was completed, the reactor was cooled to 50°C, depressurized, and the contents removed.

For highly polar media (e.g.,  $\text{ZnCl}_2$ /methanol), the products were diluted with methanol to ensure dissolution of any nitrogen complexes. A sample of the product was then removed and extracted with aqueous hydrochloric acid. The organic layer from this extraction was then extracted with aqueous sodium hydroxide, dried, and analyzed by gas chromatography. The aqueous layer of the first extraction was made basic by adding a stoichiometric excess of NaOH (solution blue to litmus paper) and was then extracted with cyclohexane. The organic layer of this extraction was analyzed by gas chromatography after first adding an internal standard.

#### D. Analytical Methods

##### 1. Soxhlet Extractions

A standard Soxhlet apparatus was used to extract approximately 2 gm of dried product successively with toluene and pyridine. According



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Fig. 9. Procedure for the Workup of the Products of the Quinoline Hydrogenation Experiments.

to Kiebler (K9), successive extractions with different solvents gives essentially the same yield as could have been obtained by the best solvent alone. The extractions were run to completion (liquid extract colorless) or until a reasonable time limit was reached. This time limit was chosen to be 6 hours for toluene extractions and 24 hours for pyridine extractions.

The liquid extracts were dried in pre-weighed Petri dishes. After most of the solvent was removed, the Petri dish was further dried in a nitrogen-purged vacuum oven at 105°C for about 12 hours. No solvent incorporation was detected for the toluene extractions. The pyridine extractions typically exhibited a 5-10% increase in weighing after drying, due to pyridine incorporation. The pyridine in the extract was estimated by assuming the increase in weight was evenly distributed over the extract and residue. Extraction yields are reported on a moisture-, ash-, and solvent-free basis.

## 2. Gas Chromatography

Liquid-phase products from the model-compound experiments were routinely analyzed by gas chromatography in a Hewlett Packard 5840A model gas chromatograph equipped with a 1/8-inch by 10-foot column packed with 3% OV-225 on chromosorb W. The column was used in a temperature programmed mode (60°C to 225°C at 10°C/min) to enhance the separation. Under these conditions, good resolution was obtained for the following compounds in the following order: cyclohexane, benzene, n-propylcyclohexane, n-propyl benzene, benzaldehyde, benzyl alcohol, 2,3-cyclohexenopyridine, N-propylaniline, quinoline, and 1,2,3,4-tetrahydroquinoline. In addition, the solvents used in these experiments could be readily separated and distinguished from the reactants and products.



The identity of the individual chromatographic peaks was determined by a comparison of elution times with standards of known composition. In addition, on selected occasions, the products were analyzed by the combined gas chromatography/mass spectrometry (GC/MS) technique. Quantitative data were obtained by introducing an accurately weighed amount of internal standard (usually m-dichlorobenzene) into the sample to be analyzed, and then calculating the ratio of areas of the standard and the component in question. This method was calibrated by making standard solutions of various weight ratios of the compounds. In practice, a plot of standard-to-test-component area ratio was plotted against standard-to-test-component weight ratio, and the weight of the test-component was simply read from the plot. This plot yielded a straight line for all of the compounds which were calibrated.

### 3. Elemental Analysis

The elemental analysis of the reaction products was determined by the U.C. Berkeley College of Chemistry Microanalytical Laboratory. The samples were submitted in sealed 1-dram vials placed inside a bottle containing desiccant. The carbon, nitrogen, and hydrogen tests were performed using a Perkin Elmer Model 240 CHN Analyzer. Metal analyses were performed by atomic absorption in a Perkin Elmer Model 360 Atomic Absorption Spectrophotometer. Oxygen could not be determined directly, and is calculated by difference.

### 4. Chemical Analysis of Vent Gas

Nitrogen components of the vent gas were determined by gas absorption into appropriate solutions. In general, amines interfere with qualitative tests for ammonia. However, the double iodide of mercury and potassium gives a reddish brown precipitate with ammonia, pale yellow

precipitates methylamine and ethylamine, and a white precipitate with propylamine and benzylamine. No precipitate forms with quinoline. The marked difference in color made possible a good qualitative analysis of the gas and a rough estimate of the ammonia present.

Nitrogen oxide gases were detected by their participation in the diazo coupling reaction between sulfanilic acid and phenylenediamine dihydrochloride. The absorbance of this solution was calibrated using standard solutions of sodium nitrite.

#### E. Experiments Performed

The experiments performed in this study are listed in Tables V, VI, VII and VIII. The oxidation experiments with model-compounds are shown in Tables V and VI. These experiments were performed in an attempt to understand what conditions would lead to nitrogen removal. Some of the effects studied were the effects of temperature, pressure, residence time, free-radical initiators, and substrate concentration. Table VII lists the experiments performed on hydrogenated coal products. These experiments were performed in an attempt to assess the effects of oxidation on hydrogenated coal products, and to compare this data with the model-compound study. Hydrogenation experiments (Table VIII) were performed in order to investigate the hydrogenation, hydrocracking, and hydrodenitrogenation activity of zinc containing catalytic systems and especially of tetralin soluble zinc compounds.

Table V. Model Compound Oxidation Experiments at 1 Atmosphere Total Pressure

Run No.	Substrate (mmoles)	Solvent (ml)	Sparging Gas	Temp. (°C)	Residence Time (hr)	Additives (mmoles)
2	Benzylamine (47.0)	Chlorobenzene (55)	O <sub>2</sub>	75	18	-
3	Benzylamine (19.0)	Chlorobenzene (55)	O <sub>2</sub>	75	18	-
4	Cyclohexene (12.0)	Chlorobenzene (25)	O <sub>2</sub>	75	18	ABN (3.2)
5	Benzylamine (9.2)	Chlorobenzene (25)	O <sub>2</sub>	75	18	ABN (1.7)
6	Benzylamine (9.2)	Chlorobenzene (25)	O <sub>2</sub>	75	18	Co(acac) <sub>3</sub> (.025)
7	Benzylamine (9.2)	Chlorobenzene (25)	O <sub>2</sub>	75	18	ABN (.42)
8	Benzylamine (9.2)	Chlorobenzene (25)	O <sub>2</sub>	75	18	ABN (0.43) Co(acac) <sub>3</sub> (.018)
9	Benzylamine (9.2)	Chlorobenzene (25)	O <sub>2</sub>	100	18	-
10	Benzylamine (27.9)	m-Dichlorobenzene (25)	O <sub>2</sub>	140	18	-
11	Benzylamine (9.2)	m-Dichlorobenzene (25)	O <sub>2</sub>	140	18	-
12	Benzylamine (9.2)	m-Dichlorobenzene (25)	O <sub>2</sub>	140	18	-
13	Benzylamine (9.2)	H <sub>2</sub> O (25)	N <sub>2</sub>	75	18	H <sub>2</sub> O <sub>2</sub> (13.0)
14	Benzylamine (9.2)	H <sub>2</sub> O (25)	N <sub>2</sub>	75	18	H <sub>2</sub> O <sub>2</sub> (13.0) H <sub>2</sub> SO <sub>4</sub> (26.0)

Table V. (continued)

Run No.	Substrate (mmoles)	Solvent (ml)	Sparging Gas	Temp. (°C)	Residence Time (hr)	Additives (mmoles)
15	Benzylamine (46.0)	m-Dichlorobenzene (25)	O <sub>2</sub>	140	18	Ni(acac) <sub>2</sub> (.029) Co(acac) <sub>3</sub> (.028) Fe(acac) <sub>3</sub> (.042)
16	Benzylamine (46.0)	m-Dichlorobenzene (25)	O <sub>2</sub>	140	20	-
17	Benzylamine (46.0)	m-Dichlorobenzene (25)	O <sub>2</sub>	140	12	Ni(acac) <sub>2</sub> (.025) Co(acac) <sub>3</sub> (.048) Fe(acac) <sub>3</sub> (.049)
18	Benzylamine (46.0)	m-Dichlorobenzene (25)	O <sub>2</sub>	140	18	Fe(acac) <sub>3</sub> (.053)
19	Benzylamine (46.0)	m-Dichlorobenzene (25)	O <sub>2</sub>	140	18	-
20	Benzylamine (46.0)	m-Dichlorobenzene (25)	O <sub>2</sub>	140	18	Co(acac) <sub>3</sub> (.037)
21	Benzylamine (46.0)	1,2,4-Trichlorobenzene (25)	O <sub>2</sub>	170	18	-
22	Benzylamine (46.0)	1,2,4-Trichlorobenzene (25)	O <sub>2</sub>	170	15	-
24	Benzylamine (46.0)	1,2,4-Trichlorobenzene (25)	O <sub>2</sub>	170	18	Fe(acac) <sub>3</sub> (.048)
25	Benzylamine (46.0)	1,2,4-Trichlorobenzene (25)	O <sub>2</sub>	190	12	-
27	Benzylamine (46.0)	1,2,4-Trichlorobenzene (25)	O <sub>2</sub>	170	12	-
30	1,2,3,4 Tetrahydro-isoquinoline (40.0)	1,2,4-Trichlorobenzene (25)	O <sub>2</sub>	170	18	-

Table VI. Benzylamine Oxidation Experiments Conducted at 100 psia Oxygen Partial Pressure

<u>Run No.</u>	<u>Substrate (mmoles)</u>	<u>Solvent (ml)</u>	<u>Temp. (°C)</u>	<u>Residence Time (hr)</u>
23	92.0	Chlorobenzene (50)	140	4.5
26	92.0	1,2,4-Trichlorobenzene (50)	140	9.5
28	92.0	1,2,4-Trichlorobenzene (50)	170	4.5
29	92.0	1,2,4-Trichlorobenzene (50)	170	2.0

Table VII. Hydrogenated Coal Oxidation Experiments at 1 atm. Total Pressure

Run No.	Substrate (gm)	Solvent (ml)	Sparging Gas	Temp. (°C)	Residence Time (hr)	Additives (gm)
31	SRC (5.0)	Quinoline (45.0)	O <sub>2</sub>	170	18.0	-
32	SRC (5.0)	H <sub>2</sub> O (25.0)	N <sub>2</sub>	75	1.0	H <sub>2</sub> O <sub>2</sub> (1.80)
33	SRC (5.0)	Quinoline (45.0)	O <sub>2</sub>	170	6.0	-
34	SRC (5.0)	Quinoline (45.0)	O <sub>2</sub>	170	0.5	-
35	SRC (5.0)	Quinoline (45.0)	O <sub>2</sub>	170	0.5	Fe(acac) <sub>3</sub> (.096)
36	SRC (5.0)	Quinoline (45.0)	O <sub>2</sub>	170	0.5	-
37	SRC (5.0)	H <sub>2</sub> O (25.0)	N <sub>2</sub>	80	1.0	H <sub>2</sub> O <sub>2</sub> (15.0)
38	SRC (5.0)	Phenylether (45.0)	O <sub>2</sub>	170	0.5	-
39	SRC (5.0)	Phenylether (45.0)	O <sub>2</sub>	170	6.0	-
40	MTC 1 (5.0)	Phenylether (45.0)	O <sub>2</sub>	170	6.0	-
41	MTC 1 (5.0)	Phenylether (45.0)	O <sub>2</sub>	170	6.0	-
42	MTC 2 (5.0)	Phenylether (45.0)	O <sub>2</sub>	170	6.0	Fe(acac) <sub>3</sub> (.098)

Table VIII. Quinoline Hydrogenation Experiments

Run No.	Reactor Contents (gm)	Temp. (°C)	Hydrogen Partial Pressure (psia)	Residence Time (hr)
43	ZnCl <sub>2</sub> (273.0) Methanol (50.0) Quinoline (5.0)	300	1000	1.0
44	90% H <sub>3</sub> PO <sub>4</sub> (250.0) Zn(PO <sub>4</sub> ) <sub>2</sub> (12.5) FeSO <sub>4</sub> (12.5) Quinoline (5.0)	300	1000	1.0
45	Tetralin (230.0) Benzoic Acid (20.0) Zinc Benzoate (12.5) Quinoline (5.0)	275	1000	1.0
46	Tetralin (230.0) Octanoic Acid (20.0) Zinc Octanoate (12.5) Quinoline (5.0)	300	1000	1.0
47	Tetralin (230.0) Quinoline (5.0)	300	1000	1.0
48	Tetralin (230.0) Quinoline (5.0)	300	800	1.0
49	Tetralin (230.) Quinoline (5.0)	300	800	1.0

Table VIII (continued)

<u>Run No.</u>	<u>Reactor Contents (gm)</u>	<u>Temp. (°C)</u>	<u>Hydrogen Partial Pressure (psia)</u>	<u>Residence Time (hr)</u>
50	Tetralin (230.0) Quinoline (5.0) Zinc Octanoate (12.5)	300	800	1.0
51	Tetralin (230.0) Octanoic Acid (20.0) Zinc Octanoate (12.5)	300	800	1.0
52	Tetralin (230.0) Zinc Oxide (12.5) Quinoline (5.0)	300	800	1.0
53	Tetralin (230.0) Quinoline (5.0)	300	800	1.0
54	Tetralin (230.0) Zinc Salicylate (12.5) Quinoline (5.0)	300	800	1.0
55	Tetralin (230.0) Zinc Phenolate (12.5) Quinoline (5.0)	300	800	1.0



Footnotes to Runs

<u>FN</u>	<u>Run</u>	<u>Note</u>
1	3	Absorbing solution lost.
2	17	Freshly distilled substrate used in this run and in all following runs.
3	21	Leak detected out of the first absorber.
4	22	Temperature drifted to 180°C.
5	27	High stirring rate used.
6	32	Bumping occurred during run.
7	36	Violent bumping during vacuum transfer.
8	44	Corrosion noted on reactor internals.
9	45	Long heatup time, temperature control difficult, temperature overshoot.
10	46	Broken liner.
11	47	Broken liner.

### III. Results and Discussion

#### A. Model-Compound Oxidation

##### 1. General Considerations

In this portion of the study, benzylamine and 1,2,3,4-tetrahydro-isoquinoline (THIQ) were oxidized under controlled conditions to determine what conditions might lead to the removal of nitrogen. Benzylamine appeared to be more reactive than THIQ, and therefore could be used to investigate more subtle changes in reaction conditions. In addition, its oxidation results in significantly less polymerization, and yields a minimum of  $\text{CO}_2$  and of amines other than ammonia. Thus, benzylamine appeared an ideal model-compound for exploratory study and it was used for most of the experiments.

Under all of the test reaction conditions, analysis of the liquid products was complicated by formation of high-molecular-weight polymeric products. These polymeric by-products appeared to involve the participation of oxygen since no polymer formed unless oxygen was present. Polymeric by-products from amine oxidation in this study were generally insoluble in the reaction media, and were not investigated. An indication of their nature is given by a comparison with the oxidation of cyclohexylamine under similar conditions, which is reported to produce 2'-cyclohexylcyclohexanespiro-3'-oxazolidine, NN'-dicyclohexyl-adipamide, N-cyclohexylamine, and N-cyclohexylidenecyclohexylamine, along with ammonia as a gaseous product (H5).

It appears that only a portion of the ammonia produced during the reaction was stripped out of the reactor and collected in the absorbing solutions. The remainder apparently reacted further, with either the substrate or its oxidation products, before it could be removed. No

nitrogen oxides were detected during the experiments. The liquid-phase product that was monitored (usually benzaldehyde) also apparently reacted further to products which were not measured.

The ammonia produced was considered to be the most dependable and reproducible indicator of amine reactivity, and it was generally used to determine the degree of success of the experiments. The non-destructive method used to measure the ammonia produced also allowed for several measurements to be taken during the reaction.

Tables IX, X, and VI list the results obtained from the benzylamine oxidation experiments. These results will be discussed below under the appropriate headings.

## 2. Effect of Temperature

Runs at 75°C with the addition of azobisisobutyronitrile (ABN) as a free-radical initiator exhibited the presence of ammonia in the vent gas (runs 5,7). Runs at 75°C using  $\text{CO}(\text{acac})_3$  did not yield appreciable amounts of ammonia (runs 6,8). The cumulative ammonia produced plotted against time for uncatalyzed runs 9, 19, 21, and 25 is shown in Figure 10. The rate of ammonia formation was accelerated by increasing the temperature between 100°C and 170°C, but no further major increase was noted on going to 190°C. However, benzaldehyde production showed a smooth increase with temperature, even to 190°C (Figure 11).

The vent-gas absorbate did not contain dissolved nitrites, indicating that little or no nitrogen oxide gas was formed during the oxidation. Apparently, any free radicals containing nitrogen are quenched by hydrogen abstracted from the substrate, rather than by interacting with molecular oxygen which has a low solubility in the liquid phase. The molar sum of ammonia extracted from the vent gas and

Table IX. Products from the Uncatalyzed Oxidation of Benzylamine at  
1 Atmosphere Total Pressure

Run No.	Residence Time (hr)	Temp. (°C)	Sparging Gas	Ammonia Produced (%)*	Benzaldehyde Produced (%)*	Residual Base (%)*
9	18	100	O <sub>2</sub>	0.3	nd	nd
10	18	140	O <sub>2</sub>	9.0	nd	nd
11	18	140	O <sub>2</sub>	3.0	5.2	84.2
12	18	140	O <sub>2</sub>	0.0	0.0	97.7
16	20	140	O <sub>2</sub>	18.6	67.5	51.0
19	18	140	O <sub>2</sub>	10.1	28.5	79.8
21	18	170	O <sub>2</sub>	32.4	39.8	7.1
25	12	190	O <sub>2</sub>	33.8	37.0	7.3
27	12	170	O <sub>2</sub>	32.1	49.8	24.5

\* (moles recovered/moles benzylamine charged) x 100

nd no data

Table X. Products from the Oxidation of Benzylamine at 1 Atmosphere Total Pressure and with Metal Salt, Free-Radical Initiator, or Peroxide Additives

Run No.	Residence Time (hr)	Additives (mmoles)	Temp. (°C)	Sparging Gas	Ammonia Produced (%)*	Benzaldehyde Produced (%)*	Residual Base (%)*
5	18	ABN (1.5)	75	O <sub>2</sub>	31.0	nd	nd
6	18	Co(acac) <sub>3</sub> (.025)	75	O <sub>2</sub>	0.2	nd	nd
7	18	ABN (0.42)	75	O <sub>2</sub>	20.0	nd	nd
8	18	ABN (0.43) Co(acac) <sub>3</sub> (.018)	75	O <sub>2</sub>	1.0	nd	nd
13	18	H <sub>2</sub> O <sub>2</sub> (13.0)	75	N <sub>2</sub>	3.2	4.5	32.1
14	18	H <sub>2</sub> O <sub>2</sub> (13.0) H <sub>2</sub> SO <sub>4</sub> (26.0)	74	N <sub>2</sub>	1.9	1.2	nd
15	18	Ni(acac) <sub>2</sub> (.029) Co(acac) <sub>3</sub> (.028) Fe(acac) <sub>3</sub> (.042)	140	O <sub>2</sub>	18.0	0.0	69.1

\* (moles recovered/moles benzylamine charged) x 100

nd no data

Table X (continued)

<u>Run No.</u>	<u>Residence Time (hr)</u>	<u>Additives (mmoles)</u>	<u>Temp. (°C)</u>	<u>Sparging Gas</u>	<u>Ammonia Produced (%)*</u>	<u>Benzaldehyde Produced (%)*</u>	<u>Residual Base (%)*</u>
17	12	Ni(acac) <sub>2</sub> (.025) Co(acac) <sub>3</sub> (.048) Fe(acac) <sub>3</sub> (.049)	140	O <sub>2</sub>	14.7	0.0	62.8
18	18	Fe(acac) <sub>3</sub> (.053)	140	O <sub>2</sub>	31.5	76.7	33.9
20	18	Co(acac) <sub>3</sub> (.037)	140	O <sub>2</sub>	25.6	0.0	51.3
24	18	Fe(acac) <sub>3</sub> (.048)	170	O <sub>2</sub>	34.7	34.2	0.6

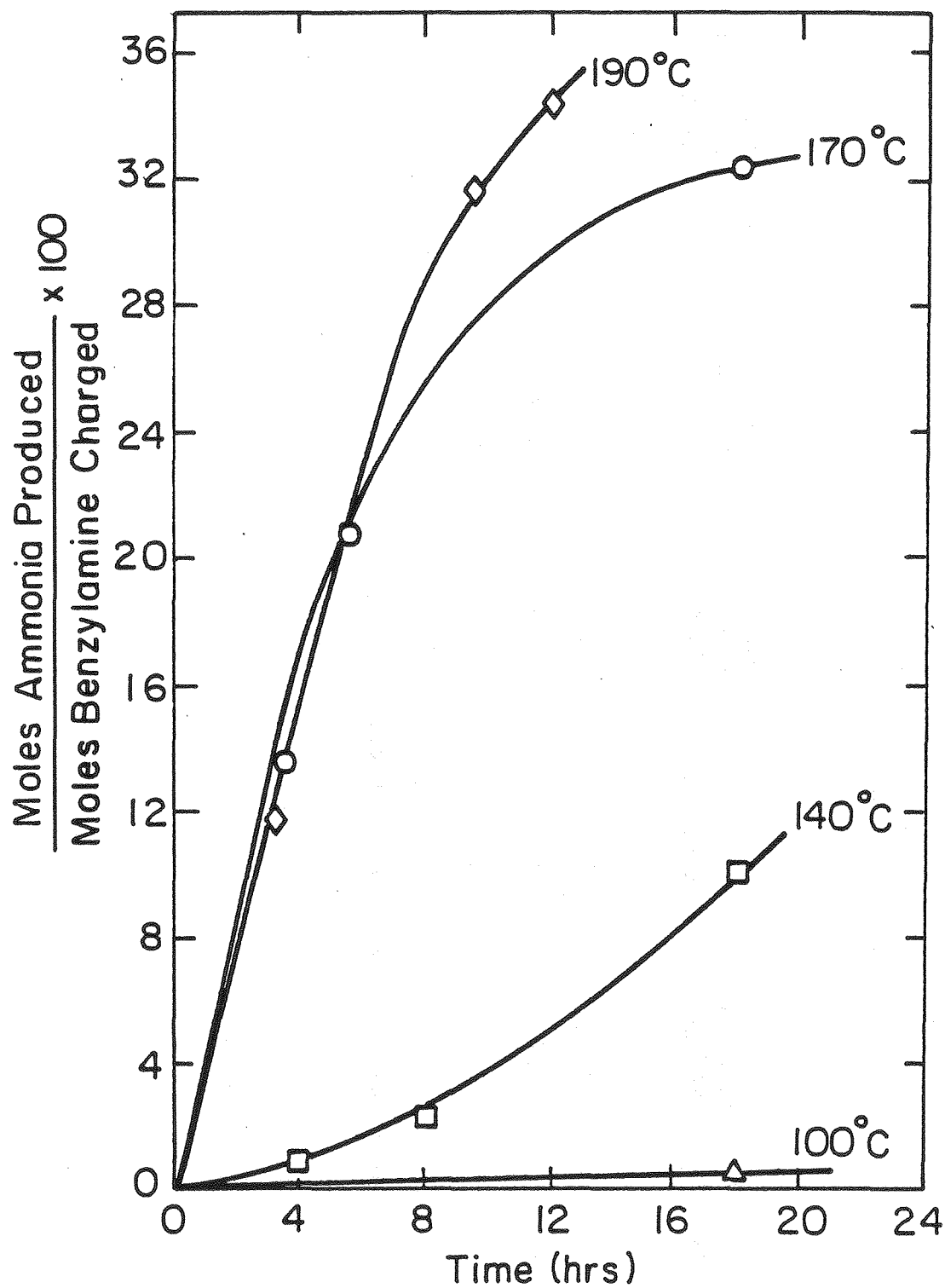
\* (moles recovered/moles benzylamine charged) x 100

nd no data

Table XI. Products from the Oxidation of Benzylamine at 100 psia  
Oxygen Partial Pressure.

<u>Run No.</u>	<u>Residence Time (hr)</u>	<u>Temp. (°C)</u>	<u>Ammonia Produced (%)*</u>	<u>Benzaldehyde Produced (%)*</u>	<u>Base Extracted from Liquid Products (%)*</u>
23	4.5	140	1.7	9.8	96.6
26	9.2	140	10.5	46.4	80.9
28	4.5	170	12.7	54.8	38.3
29	2.0	170	8.8	50.0	43.8

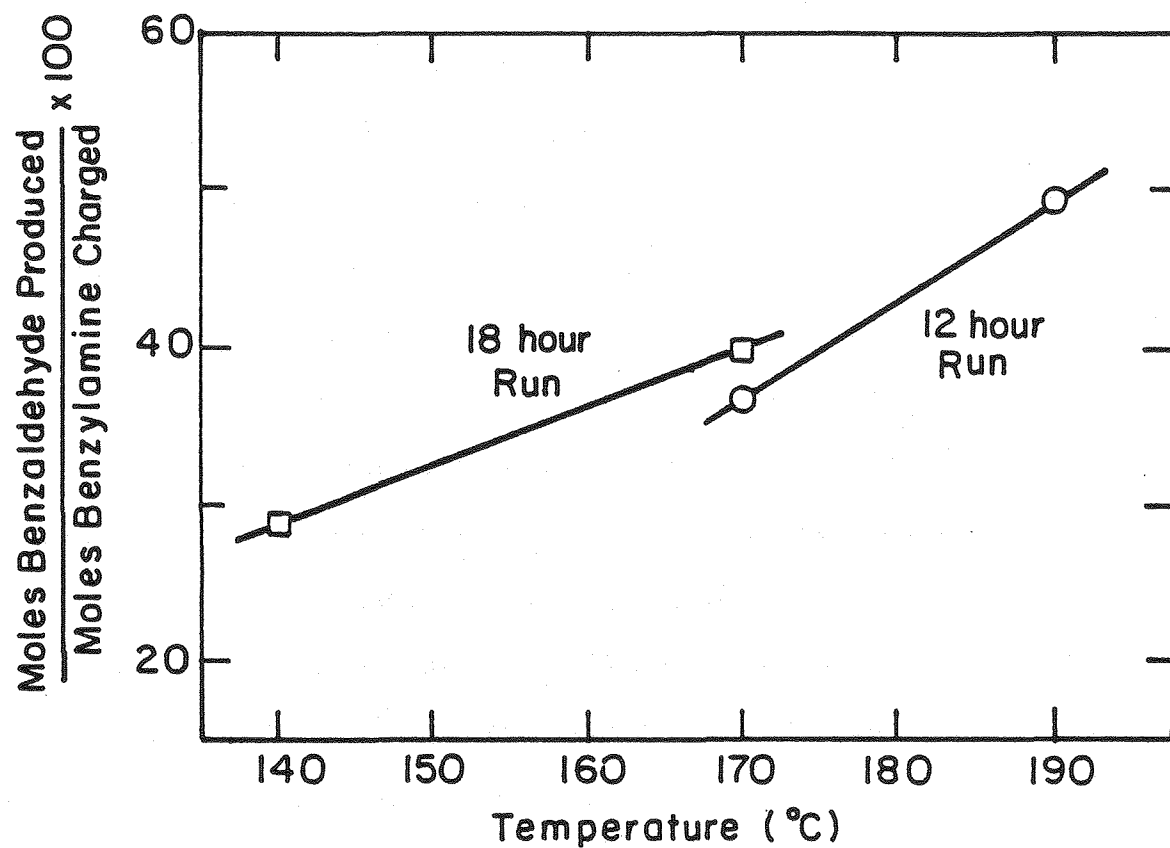
\*  
(moles recovered/moles benzylamine charged) x 100



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Fig. 10 Effect of Temperature on Ammonia Production During the Oxidation of Benzylamine (1 Atm. Total Pressure).





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Fig. 11. Effect of Temperature on Benzaldehyde Production During the Oxidation of Benzylamine.

of base extracted from the liquid products is usually less than the moles of original amine, suggesting that significant amounts of amine and ammonia entered into the production of polymeric material.

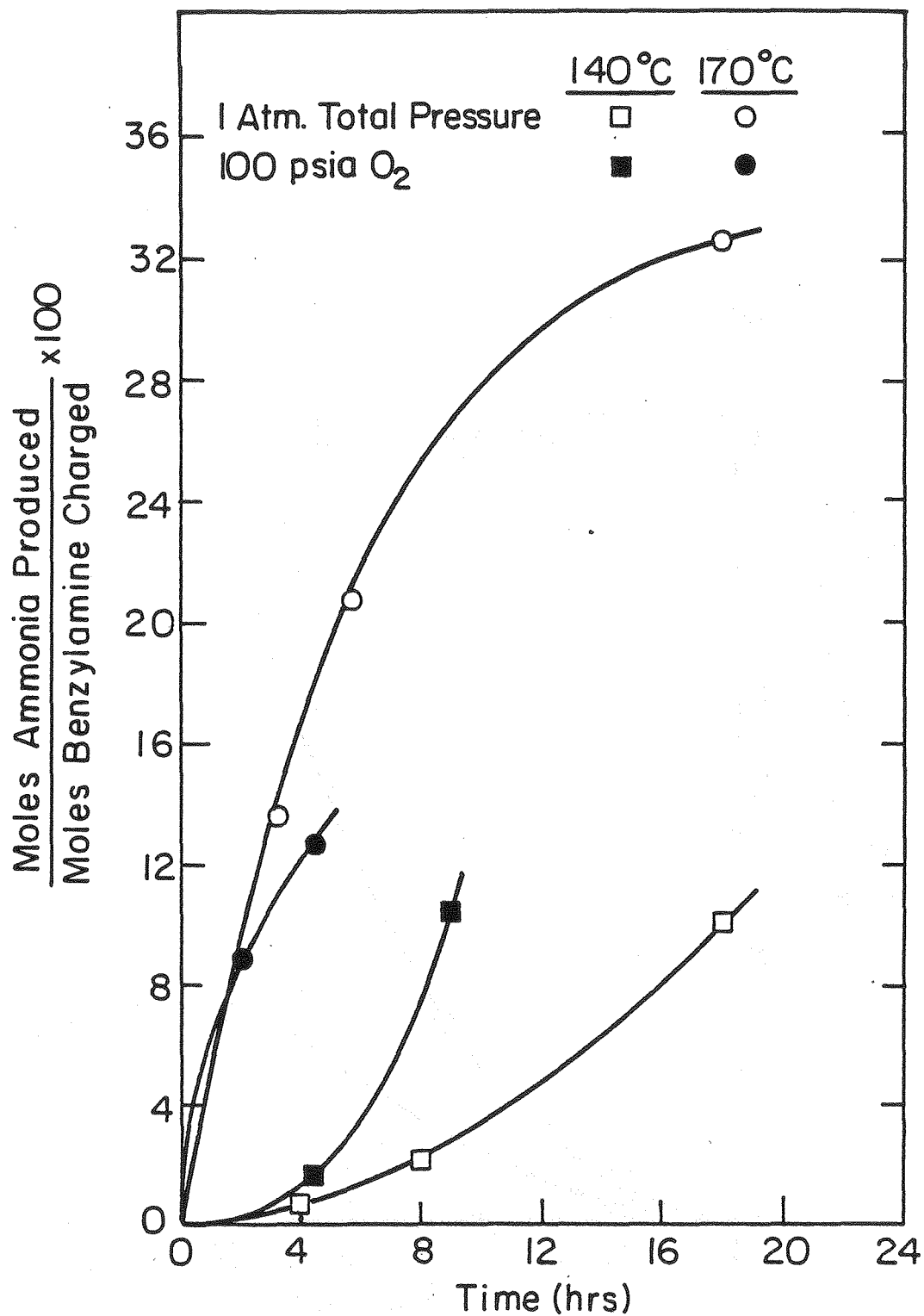
### 3. Effect of Pressure

Previous work on liquid phase oxidation of both pure hydrocarbon and on nitrogen-containing substrates has shown that the rate of oxidation is zero order in oxygen partial pressure when the reaction is initiated by free-radical initiators and is not allowed to proceed beyond a few percent conversion (V2). However, under conditions when the reaction is thermally initiated, the rate can be expected to depend on oxygen partial pressure.

Data for runs 23, 26, 27, 28, and 29 are shown in Figure 12. Ammonia production increased with pressure strongly at 140°C and less strongly at 170°C. Aldehyde production seems to be even more dependent on oxygen pressure, and significant yields of aldehydes in relatively short times were observed at high pressure (Table XI). The pressure runs exhibited the largest discrepancy between ammonia and aldehyde produced, presumably because the ammonia was held in contact with the liquid phase until the reaction terminated, thereby allowing for further reaction of the ammonia.

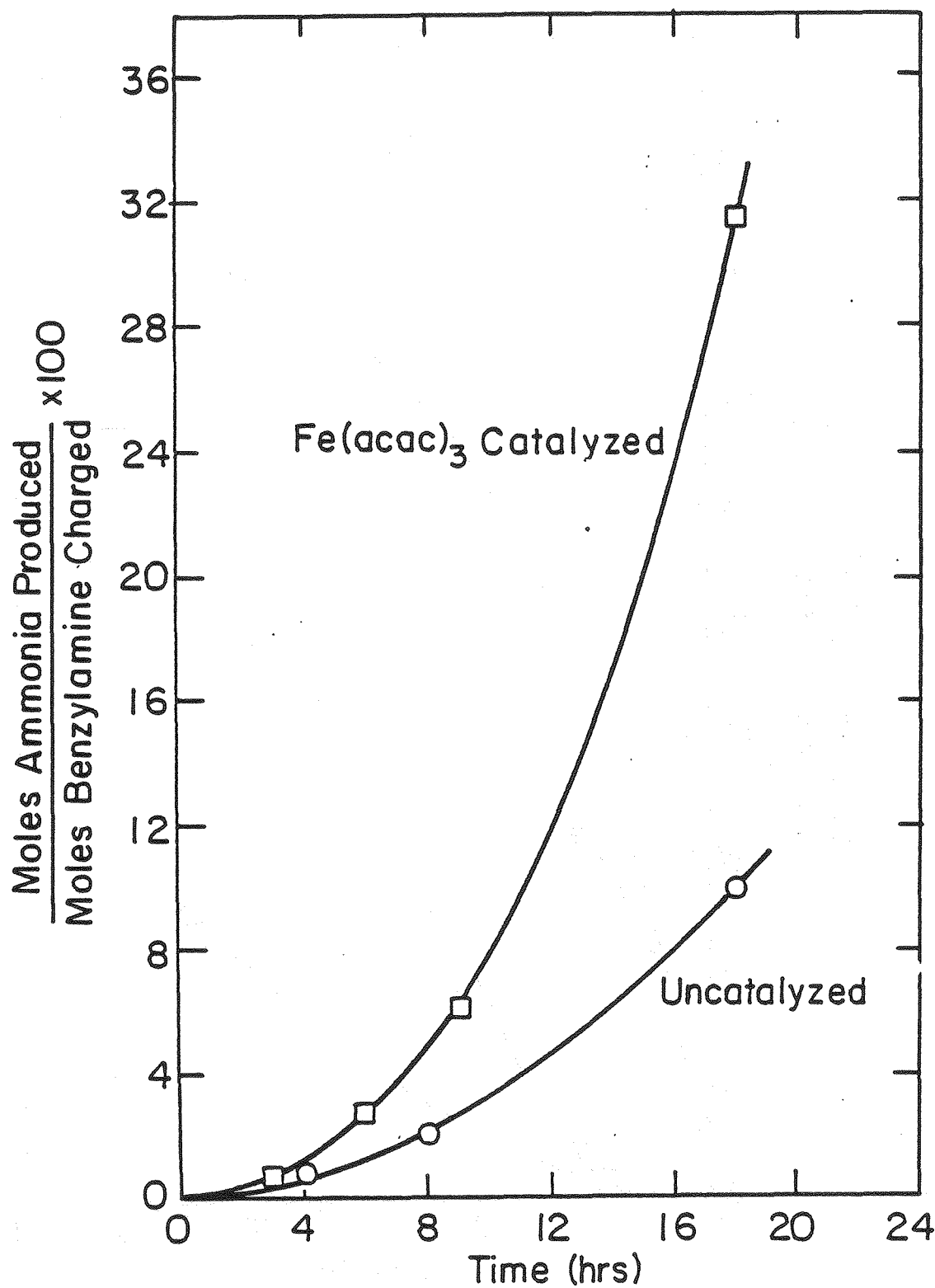
### 4. Effect of Metal Salts

Under the conditions used in this study, both  $\text{Co}(\text{acac})_3$  and  $\text{Fe}(\text{acac})_3$  accelerated the production of ammonia from the reactor (Figure 13 and 14).  $\text{Co}(\text{acac})_3$  appeared to be the best catalyst, at least at 140°C. The iron salt also increased the formation of benzaldehyde. However, when cobalt salts were present in the reaction mixture, either alone or in combination with nickel or iron, no aldehydes were



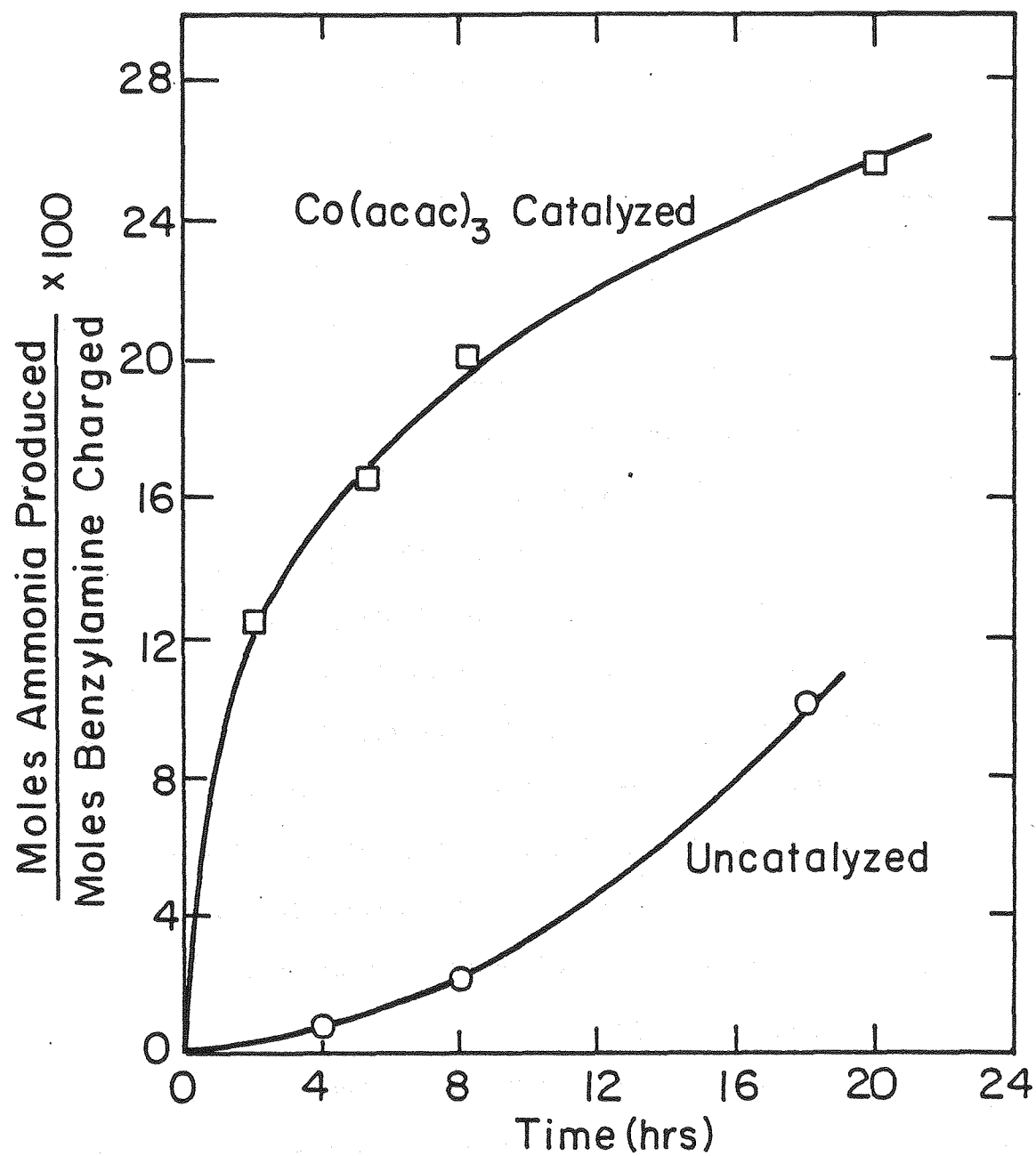
XBL 807-5430

Fig. 12. Effect of Pressure on the Production of Ammonia During the Oxidation of Benzylamine.



XBL 807-5431

Fig. 13. Effect of  $\text{Fe}(\text{acac})_3$  on the Production of Ammonia from Benzylamine ( $140^\circ\text{C}$ , 1 Atm. Total Pressure).



XBL 807-5432

Fig. 14. Effect of  $\text{Co}(\text{acac})_3$  on the Production of Ammonia from Benzylamine ( $140^\circ\text{C}$ , 1 Atm. Total Pressure).

detected. Apparently aldehydes are oxidized further in the presence of cobalt.

### 5. Effect of Hydrogen Peroxide

Hydrogen peroxide, alone and mixed with sulfuric acid, was used in runs 13 and 14. The results of these experiments indicate that the oxidation of benzylamine with hydrogen peroxide produces aldehydes and ammonia as major reaction products, and therefore appears to be chemically similar to oxidation with molecular oxygen. However, the yields under the conditions studied were quite small.

### B. Hydrogenated Coal Oxidation

#### 1. General Considerations

In this portion of the study, the effect of oxidation on the nitrogen content and solvent solubilities of coal-derived materials was investigated. The results of the model-compound study were used as a guide for determining the conditions most likely to succeed. Three materials were selected for this study: solvent-refined coal (SRC), and two types of melt-treated coal (MTC 1, MTC 2). The analyses of these materials is given in Table IV. The oxidation results are shown in Table XII, and are discussed under the appropriate headings below.

#### 2. Effect of Solvent

An ideal solvent for carrying out the oxidation experiments would be one which completely dissolves the hydrogenated coal, does not oxidize under the conditions studied, does not incorporate to any great extent, has a high boiling point, and is liquid at room temperature. Several of the experiments on hydrogenated coals (31, 33, 34, 35, 36) were performed with quinoline as a solvent. These runs in general exhibited a substantial increase in nitrogen content, oxygen content,

Table XII. Analysis of Products from the Oxidation of Hydrogenated Coals at  
1 Atmosphere Total Pressure.

Run No.	Substrate (% by wt.)	Additives (gm)	Residence Time (hr)	Temp. (°C)	Recovery (%)	Product Analysis*						Gas Anal.	
						%C	%H	%N	Tol. Sol.	Pyr. Sol.		NH <sub>3</sub>	NO <sub>2</sub>
31	SRC (10)	-	18.0	170	122.7	79.4	4.26	4.56	8.0	30.0		tr	-
33	SRC (10)	-	6.0	170	122.0	79.4	4.19	4.09	.3	33.4		tr	-
34	SRC (10)	-	0.5	170	105.7	86.0	5.20	3.36	38.0	93.0		-	-
35	SRC (10)	Fe(acac) <sub>3</sub> (.096)	0.5	170	105.6	85.4	5.13	2.94	5.4	82.5		-	-
36	SRC (10)	-	0.5	170	103.3	85.7	5.30	3.72	48.0	96.8		-	-
37	SRC (6.3)	H <sub>2</sub> O <sub>2</sub> (15.0)	1.0	80	95.0	80.9	5.70	2.16	60.6	96.4		-	-
38	SRC (10)	-	0.5	170	97.6	85.4	5.17	2.08	12.6	94.6		-	-
39	SRC (10)	-	6.0	170	105.9	79.7	4.17	2.04	11.5	60.1		tr	-
40	MTC 1 (10)	-	6.0	170	103.6	67.3	4.57	0.73	14.2	45.5		tr	-
41	MTC 2 (10)	-	6.0	170	99.1	63.1	5.10	0.73	25.5	71.6		tr	-
42	MTC 2 (10)	-	6.0	170	99.7	63.2	4.96	0.70	20.0	55.6		tr	-

\* wt.-%, MAP, solubilities are corrected for solvent incorporation

tr trace

and total weight, presumably due to solvent incorporation and oxygen uptake. Experiments using phenylether as a solvent (38, 39, 40, 41, 42) exhibited a significantly smaller amount of solvent incorporation. The fact that the preasphaltene content of the oxidized products is larger with phenylether as a solvent than with quinoline may mean that the ether solvent is less effective in dissolving preasphaltenes, which then react as a slurry rather than a true solution.

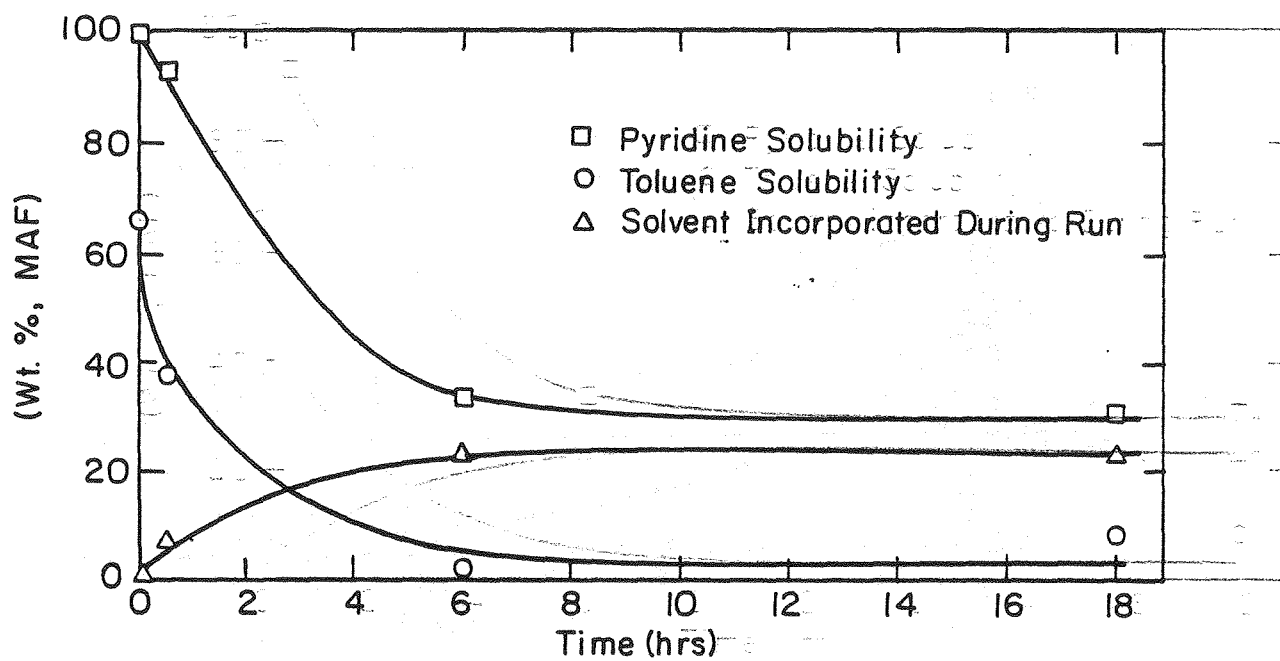
### 3. Effect of Oxidation on Product Solubility

The solubilities of the hydrogenated coals in pyridine or toluene are reduced by low-temperature oxidation, as illustrated in Figure 15 for SRC oxidation at 170°C. The decrease in solubility and the increase in product weight seem to take place mainly during the first 6 hours of oxidation. Reduced solubilities probably result from a combination of increased polarity from oxygen-containing functional groups, and from polymerization of more soluble fragments into less soluble polymers. The initial increase in preasphaltene content (Figure 16) strongly suggests that a significant amount of asphaltene is oxidized to preasphaltene which then reacts further to form pyridine-insoluble char.

### 4. Effect of Metal Salts

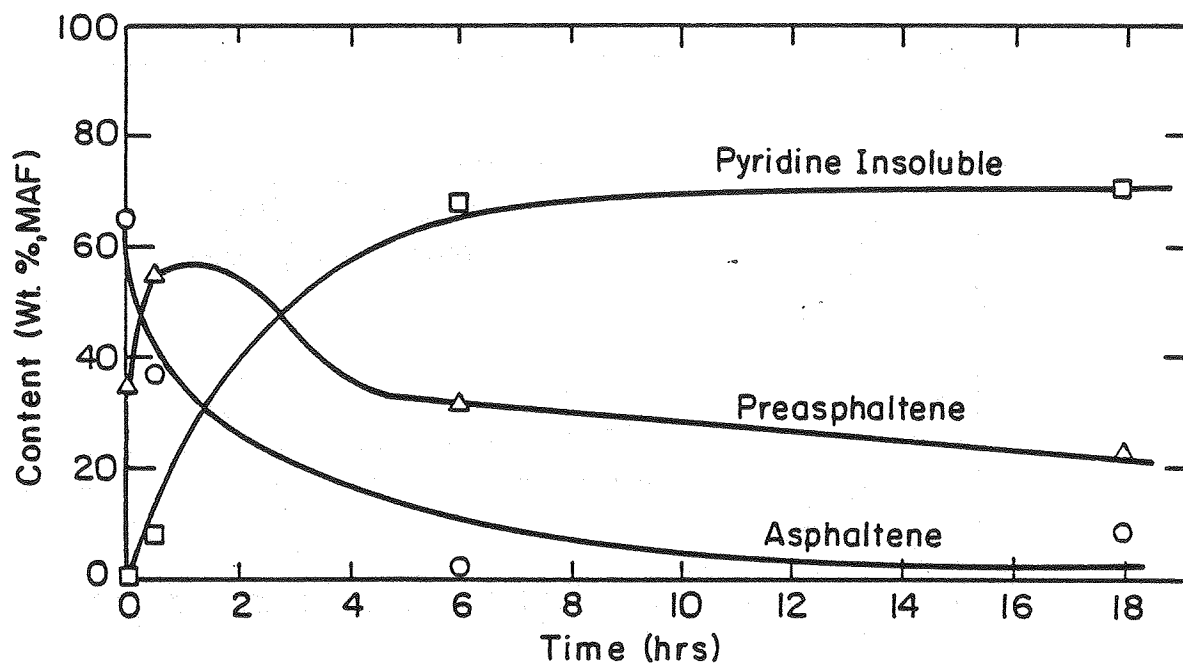
Metal salts appear to increase the rate of oxidation, especially of the asphaltene portion of the hydrogenated coals. This is shown by the reduced asphaltene content in experiments 35 and 42. The rate of disappearance of preasphaltene increases less, probably because preasphaltenes are being continually produced as well as consumed, and because preasphaltenes contain a smaller amount of easily oxidized hydroaromatic structures.





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Fig. 15. Effect of Oxidation on the Solubility of SRC (170°C, 1 Atm. Total Pressure, Quinoline Solvent).



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Fig. 16. Effect of Oxidation on Asphaltene, Preasphaltene, and Pyridine Insoluble Content of SRC (170°C, 1 Atm. Total Pressure, Quinoline Solvent).

## 5. Effect of Oxidation on Elemental Analysis

Elemental analysis of the hydrogenated coals was significantly altered during the oxidation experiments. Both carbon and hydrogen content of the feed materials were reduced due to solvent incorporation, oxygen uptake, and liberation of  $H_2O$ ,  $CO$ , and  $CO_2$ . For experiments conducted with quinoline as a solvent, a substantial increase in nitrogen content was observed. Analysis of the vent-gas absorbate for these runs shows that only small amounts of nitrogen-containing gases were produced, and very little denitrogenation took place. For the experiments performed with phenylether as a solvent, little or no evolution of nitrogen gases occurred, and only small changes in nitrogen content were observed for the products.

A plot of hydrogen content versus carbon content for the oxidized products of the three feed materials is shown in Figure 17. The reduction in hydrogen content per unit reduction in carbon content per unit reduction in carbon content appears to be higher for the melt-treated coals than the SRC. This probably reflects the higher initial H/C ratio in the melt-treated coals.

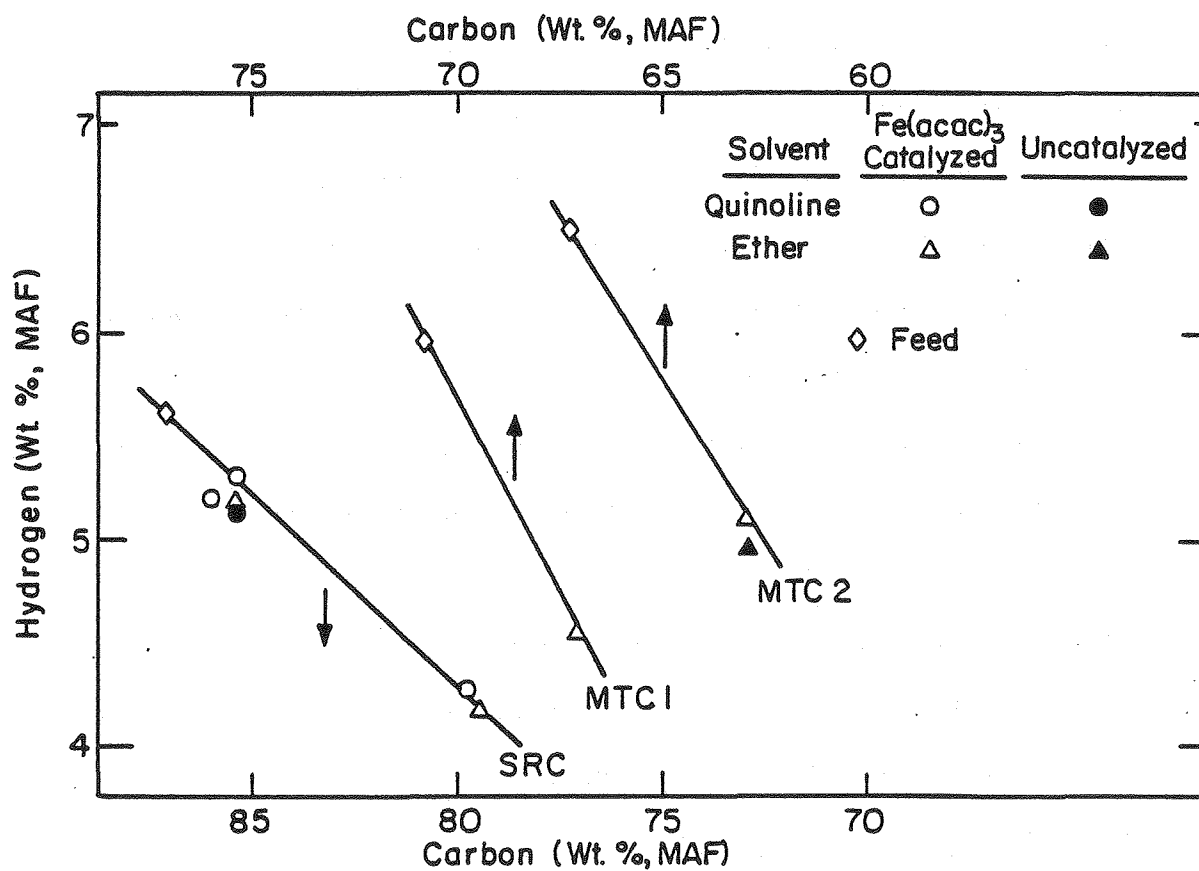
### C. Quinoline Hydrogenation

#### 1. Results of Experiments

The experiments in this portion of the study were conducted in order to investigate the hydrogenation activity of various zinc-containing catalytic systems. The results of these experiments are shown in Table XIII, and are discussed under the appropriate headings below.

#### 2. Inorganic Systems

Two inorganic systems, zinc chloride/methanol, and zinc phosphate/phosphoric acid, were studied. In the zinc chloride run, the quinoline



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Fig. 17. Hydrogen Content vs. Carbon Content for the Oxidation Products of Hydrogenated Coals.

quinoline apparently polymerized to unidentifiable high-molecular-weight material, and no hydrogenated or hydrocracked products were detected. In the phosphoric acid experiment, some hydrogenation of the heterocyclic ring in quinoline was observed, but no hydrocracking was evident. The high concentration of phosphoric acid used proved to be highly corrosive, and use of this system was not continued.

### 3. Organic Systems

Several tetralin-soluble zinc salts were screened for their hydrogenation catalytic activity. Runs 48 and 49 indicate that there may be some question of reproducibility in these experiments, since these two identical uncatalyzed runs had conversions of 32% and 20% respectively. However, due to the preliminary nature of these data, it was felt that the reproducibility was good enough to evaluate gross changes in catalytic activity.

Tetralin-soluble zinc salts reduced the amount of hydrogenation of quinoline to 1,2,3,4-tetrahydroquinoline (runs 50, 51, 54, 55). No hydrocracking or nitrogen removal was observed in any of these runs. The addition of organic acids (run 51) apparently did not change the amount of hydrogenation or hydrocracking. For cases where hydrogenation was observed, only the nitrogen-containing ring was hydrogenated. No formation of naphthalene from the tetralin solvent was observed and it seems apparent that the source of hydrogen needed for the production of hydroquinolines comes from molecular hydrogen. In support of this conclusion, it should be noted that no conversion was observed when molecular hydrogen was absent (run 53).

These experiments seem to indicate that zinc-containing salts in tetralin exhibit an inhibiting effect towards quinoline hydrogenation.

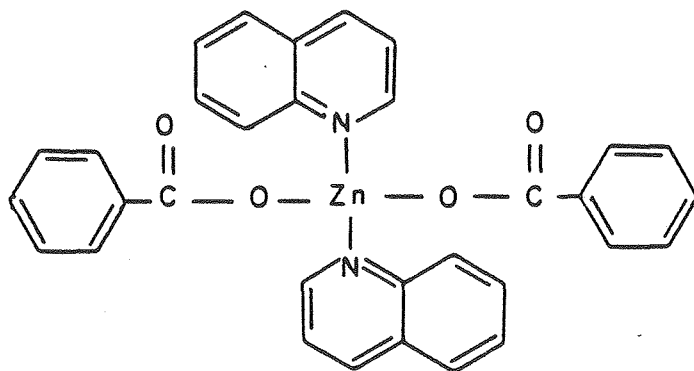
Table XIII. Products from the Hydrogenation of Quinoline

Run No.	Reactor Contents (gm)	Temp. (°C)	Hydrogen Partial Pressure (psia)	Product. Anal. (molar %)		Products Anaccounted for (molar %)
				Quinoline	THQ	
43	ZnCl <sub>2</sub> (273.0) Methanol (50.0) Quinoline (5.0)	300	1000	-	-	100
44	90% H <sub>3</sub> PO <sub>4</sub> (250.0) Zn(PO <sub>4</sub> ) <sub>2</sub> (12.5) FeSO <sub>4</sub> (12.5) Quinoline (5.0)	300	1000	85	15	35
48	Tetraline (230.0) Quinoline (5.0)	300	800	68	32	10
49	Tetralin (230.0) Quinoline (5.0)	300	800	80	20	8
50	Tetralin (230.0) Zinc Octanoate (12.5) Quinoline (5.0)	300	800	95	5	1
51	Tetralin (230.0) Octanoic Acid (20.0) Zinc Octanoate (12.5) Quinoline (5.0)	300	800	95	5	10
52	Tetralin (230.0) Zinc Oxide (12.5) Quinoline (5.0)	300	800	72	28	6

Table XIII (continued)

Run No.	Reactor Contents (gm)	Temp. (°C)	Hydrogen Partial Pressure (psia)	Product Anal. (molar %)		Products Unaccounted for (molar %)
				Quinoline	THQ	
53	Tetralin (230.0) Quinoline (5.0)	300	-	100	-	17
54	Tetralin (230.0) Zinc Salicylate (12.5) Quinoline (5.0)	300	800	93	7	5
55	Tetralin (230.0) Zinc Phenolate (12.5) Quinoline (5.0)	300	800	93	7	37

It seems plausible that the zinc may coordinate with quinoline and thereby protect it from hydrogenation by reducing the electron density in the heterocyclic ring as illustrated below.





#### IV. Conclusions

The data presented in this study are exploratory and preliminary in nature. The mechanisms for model-compound oxidation, model-compound hydrogenation, and hydrogenated coal oxidation are undoubtedly complex; no attempt at a kinetic study has been undertaken. In addition, there appear to be limitations for the data obtained. Nevertheless, these data can be used to evaluate the feasibility of the chemical processes that have been investigated.

It seems evident that nitrogen can be removed from some compounds by oxidation. However, oxidation does not appear to remove nitrogen from those compounds most representative of hydrogenated coal (e.g., 1,2,3,4-tetrahydroisoquinoline). The additional C-N bond in these compounds probably plays a major role in reducing the observed yields.

The oxidation of hydrogenated coals does not appear to produce appreciable amounts of nitrogen-containing gases, and therefore the functionalities that lead to nitrogen removal in model-compounds (primary amines) probably do not exist to any great extent in hydrogenated coals. Instead, aromatic (quinoline) and hydroaromatic (1,2,3,4-tetrahydroquinoline) functionalities probably predominate. The oxidation of hydrogenated coals also leads to a significant decrease in solubility. Therefore, the use of oxygen must be selective to prevent the undesired degrading of products into less soluble forms. It is not at all apparent that this type of selectivity is attainable.

The experiments concerning the hydrogenation activity of tetralin-soluble zinc salts indicate that these salts may reduce the rate of homogeneous hydrogenation, as compared to the uncatalyzed reaction. The complexing of the nitrogen in the substrate to zinc may

be responsible for this inhibition. The source of hydrogen for this reaction appears to be exclusively molecular hydrogen.

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